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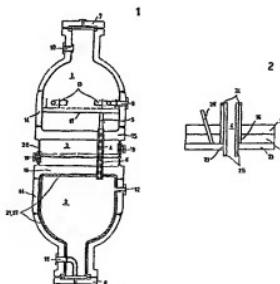
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(54) Title: TUBE BUNDLE APPARATUS FOR PROCESSING CORROSIVE FLUIDS



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(57) Abstract: Tube bundle apparatus for thermal exchange operations at high pressures and temperatures, under conditions of high aggressiveness of the process fluids, wherein the tube bundle comprises a series of tubes (4) whose internal wall is essentially constituted by a material selected from titanium, zirconium or an alloy of one of these, resistant to the aggression of said fluids, in which at least one of the access chambers to the tube bundle is DELIMITED by a wall comprising at least the following three metallic layers in succession: a) an external layer (21) suitable for tolerating the pressure load, subject to corrosion by contact with said highly aggressive process fluid; b) an intermediate layer (22) made of stainless steel; (c) an anticorrosive lining (23) in contact with said highly corrosive fluid, consisting of a material selected from titanium, zirconium or an alloy of one of these. Said apparatus is particularly used as ex-changer/reactor, for example as a stripper, in the high pressure cycle of synthesis processes of urea.



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## TUBE BUNDLE APPARATUS FOR PROCESSING CORROSIVE FLUIDS

The present invention relates to a tube bundle apparatus for processing corrosive fluids.

More specifically, the present invention relates to a tube bundle apparatus of the type with lining, suitable for processing corrosive fluids at medium or high pressures and temperatures, up to 100 MPa and 400°C respectively, especially in industrial plants for the production of urea.

The construction technique of high pressure apparatuses, whether they be reactors, separators, boilers, and other equipment in which there is a high thermal exchange, normally comprises the assembly of a compact pressure-resistant body capable of tolerating the operating pressures, guaranteeing the maximum safety and duration with time of the mechanical specifications, equipped with the necessary passages for external communication and control and the entrance and exit of the process fluids. The most widely-used material for this construction is carbon steel, due to its excellent combination of optimum mechanical properties, its rela-

tively low cost and commercial availability. In order to maximize the exchange surface, a tube bundle is usually inserted inside the pressure-resistant body, terminating, on each end, with a plate or perforated drum 5 situated on a fluid collection or distribution chamber. The thermal exchange takes place with a second fluid circulating in a chamber outside the tube bundle, in contact with the external surface of the tubes.

In processes which generate highly aggressive fluids, at least one of the two surfaces of each tube and 10 tube sheet plate and at least a part of the internal surface of the pressure-resistant body are exposed to direct contact with a process fluid having highly aggressive characteristics. Some of the methods and equipment generally used for obtaining thermal exchange 15 in these cases are provided, for example, in the technical publication "Perry's Chemical Engineering Handbook", McGraw-Hill Book Co., 6<sup>th</sup> Ed. (1984), pages 11-18.

The problem of corrosion has been faced with various solutions in existing industrial plants, and others have been proposed in literature. There are in fact numerous metals and alloys capable of resisting for sufficiently long periods the extremely aggressive conditions which are created inside a synthesis reactor of 20 25

urea or other apparatuses in processes involving highly corrosive fluids, such as in the synthesis of nitric acid, for example. Among these, lead, titanium, zirconium and several stainless steels such as AISI 316L  
5 steel (urea grade), INOX 25/22/2 Cr/Ni/Mo steel, special austeno-ferritic steels, austenitic steels with a low content of ferrite, etc., can be mentioned. An apparatus of this type however would not be economically convenient if it were entirely constructed with these  
10 corrosion-resistant alloys or metals, not only due to the considerable quantity of costly materials which would be necessary for the purpose, but also as a result of structural and construction problems due to the necessity of using special welding and bonding methods  
15 and, in certain cases, to the lack of certain metallic materials having the excellent mechanical qualities of carbon steel.

Resort is usually made to containers or columns made of normal carbon steel, optionally multilayer,  
20 having a thickness varying from 30 to 450 mm, depending on the geometry and pressure to be resistd (pressure-resistant body), whose surface in contact with corrosive or erosive fluids is uniformly covered with a metallic anticorrosive lining from 2 to 30 mm thick.

25 For example, the processes for the production of

urea normally used in industry comprise at least one section which operates at a high temperature and pressure (synthesis cycle or loop), at which the process fluids, i.e. water, ammonia and especially saline solutions, containing ammonium carbamate and urea, become particularly aggressive. It is known that normal carbon steel is not capable of resisting the corrosion of these high temperature fluids and when in contact with these, undergoes a progressive and rapid deterioration which weakens its structure causing external losses or even explosions.

In particular, in the production processes of urea currently in use, the ammonium carbamate (hereafter abbreviated with the term "carbamate", as used in the specific field) not transformed into urea is further decomposed to ammonia and carbon dioxide in the so-called high pressure stripper, substantially operating at the same pressure as the reactor and at a slightly higher temperature, which consists of a tube bundle exchanger vertically positioned, in which the solution of urea leaving the reactor and containing non-reacted carbamate and excess ammonia, is sent in a thin layer along the inside of the tubes, whereas medium pressure saturated steam (1-3 MPa) is circulated and condensed, at the temperatures indicated in the project documents,

in the chamber outside the tube bundle, to supply the necessary energy for the flash of excess ammonia and decomposition of the carbamate. The pressure-resistant body of the stripper is made of normal carbon steel,  
5 whereas the tubes of the tube bundle are generally made of a material resistant to corrosion.

The gases leaving the stripper are usually recon-  
densed in a condenser of the carbamate, also essen-  
tially consisting of a tube bundle exchanger, which is  
10 therefore in contact with a mixture similar to that of  
the decomposer (except for urea) and consequently ex-  
tremely corrosive. Also in this case the internal lin-  
ing and tube bundle are made of the above-mentioned  
particular stainless materials.

15 Production processes of urea which use the above  
separation and recondensation method of the high pres-  
sure carbamate are described, for example, in patents  
U.S. 3,984,469, U.S. 4,314,077, U.S. 4,137,262, EP  
504,966, all assigned to the Applicant. A wide range of  
20 processes normally used for the production of urea is  
also provided in "Encyclopedia of Chemical Technology",  
3<sup>rd</sup> Edition (1983), Vol. 23, pages 548-574, John Wiley &  
Sons Ed., whose contents should be referred to for fur-  
ther details.

25 In the particular case of a tube bundle thermal

exchanger, such as the stripper or carbamate condenser forming part of the synthesis cycle (loop) of urea, the solution to problems of corrosion is quite complex due to the particular geometry of the equipment which does  
5 not allow a controlled and reproducible distribution of the temperatures and compositions of the fluids, especially when the thermal exchanger is concomitant with chemical reactions. Also in these cases, attempts have been made to prevent corrosion with suitable surface  
10 linings of the tube sheet plate and other surfaces in contact with the corrosive fluids, with relative success, but so far without managing to produce an apparatus at reasonable costs, which can be run for sufficiently long times with no extraordinary maintenance.

15        It is also known that the resistance to corrosion of stainless steels in contact with acid or alkaline saline solutions, such as those of carbamate in water, is considerably increased if these fluids contain a small quantity of oxygen, introduced as air or another  
20 compound capable of generating oxygen, such as ozone or a peroxide. This technology has been widely used and is described, for example, in the patent U.S. 2,727,069 (Stamicarbon) and U.S. 4,758,311 (to the Applicant). Although providing a significant improvement, this  
25 technical solution however still has a few disadvan-

tages, due to the greater control necessary for avoiding the formation of areas with a concentration of oxygen close to the explosivity limits, and also because the distribution of oxygen is not uniform, especially  
5 in the presence of biphasic gas/liquid systems such as those present in the whole synthesis cycle of urea, and it consequently does not guarantee a satisfactory protection from corrosion in any point of the surface exposed.

10 Alloys and metals with an higher corrosion resistance than stainless steel, have already been proposed before as heavy-duty materials for the production of reactors for the synthesis of urea. For example, UK 1.046,271 (Allied Chemical Corp.) describes a process  
15 for the direct synthesis of urea at 205°C and 27 MPa in which the reactor is completely made of zirconium. It is evident however that this type of reactor implies high costs and construction difficulties.

Synthesis reactors of urea made of carbon steel  
20 lined with zirconium or titanium are mentioned in the publication "Chemical Engineering" of May 13 1974, pages 118-124, as an alternative to the reactors lined with stainless steel.

Also known are tube bundle exchanger with tubes  
25 comprising titanium or zirconium. U.S. patent 4,899,813

(assigned to the Applicant) describes the construction and use of vertical tube bundle equipment especially suitable for the high pressure stripping of the solution of urea coming from the synthesis reactor. In order to prevent corrosion in the areas inside the tubes, where the thermal exchange and decomposition of the carbamate take place and where the aggressiveness of the fluid is therefore at its maximum, a tube bundle made up of bimetallic tubes has been used, i.e. consisting of an external part made of INOX steel, and an internal very fine part, (0.7-0.9 mm) made of zirconium, attached but not welded to the former. The remaining part of the exchanger/stripper in contact with the urea solution is, on the other hand, constructed with the normal carbon steel technique lined with a suitable stainless steel. This solves problems linked to corrosion inside the tubes, due to the excellent resistance of zirconium, without however creating difficulties associated with the production of special steel/zirconium junctions which cannot be efficiently welded directly to each other, and at the same time maintaining an economic production of the equipment.

In spite of the excellent results obtained with this latter technology, it has been found however that in certain areas of the exchanger, especially concen-

trated around the lower tube sheet plate of the stripper and in the corresponding chamber, unexpected corrosion phenomena still occur under extremely aggressive conditions of the fluids. The same problem may also 5 arise, over a long period of time, in other tube bundle apparatuses operating under similar conditions of aggressiveness.

The entire lining of said equipment, however, with zirconium, titanium or one or their alloys creates considerable applicative problems, both in terms of construction engineering due to the lack of homogeneity of the welded joints, and also from the point of view of safety, as the weep-hole expedient, even if used according to the known art, would lead, after leakage of 10 the lining, to the direct contact of the corrosive fluid with the underlying carbon steel, rapidly causing structural damage, sometimes even before the loss can 15 be observed.

The problem of the life of pressure equipment exposed to extremely corrosive fluids, especially with 20 respect to the tube bundle apparatuses used in the synthesis cycle of urea, has consequently still not been solved in a satisfactory manner.

During its activities aimed at continuously improving 25 its technology, the Applicant has now found

that the above problems relating to tube bundle apparatuses, with tubes comprising an anticorrosive material different from stainless steel, can be surprisingly overcome by adopting a particular type of multilayer lining of the non-tube part exposed to corrosion fluids. This new approach also allows a reduced quantity of heavy-duty anti-corrosive material to be used for the lining, significantly increasing however the operative life of the equipment.

10 A first object of the present invention therefore relates to a tube bundle apparatus suitable for efficiently effecting the thermal exchange, under high pressure and temperature conditions, between at least two fluids of which one has highly aggressive characteristics under the process conditions, comprising a hollow body equipped with an external casing, or pressure-resistant body, suitable for tolerating the operating pressures and consisting of a material subject to corrosion by contact with said highly aggressive fluid,

15 and appropriate openings for the entrance and exit of the fluids, inside which there are at least two cavities separated from each other by a third sealed cavity with respect to these, situated between two septa or plates hinged onto the pressure-resistant body, said

20 two cavities communicating with each other by means of

25

a series of tubes, whose internal wall is put in contact with said highly aggressive fluid and consists of a material selected from titanium, zirconium or an alloy of one of them which is highly resistant to corrosion, forming a tube bundle situated between said two septa which passes through said third cavity, characterized in that at least one of said two cavities is in contact with said highly aggressive fluid and is at least partly delimited by a wall comprising at least 10 three metallic layers consisting of:

- A) an external layer suitable for tolerating the pressure load, subject to corrosion by contact with said highly aggressive process fluid;
- B) an intermediate layer made of stainless steel,;
- 15 C) an anticorrosive layer in contact with said highly corrosive fluid, consisting of a material selected from titanium, zirconium or an alloy of one of them.

A second object of the present invention relates 20 to a method for the production of said apparatus.

Other objects of the present invention will be evident for experts in the field from the present description provided hereafter.

The term "alloy of" as used herein with reference 25 to a certain metal, refers to an alloy comprising said

metal in a quantity of at least 40% by weight.

In accordance with the present description, the term "corrosion resistant" referring to a material with respect to a fluid under certain process conditions, 5 defines a material having a corrosion of less than 0.1 mm/year measured according to the regulation ASTM A 262 section C HUEY TEST, particularly adopted for current linings made of 25/22/2 stainless steel. Corrosion indexes for materials of normal industrial use are provided in various handbooks known to experts in the field, such as, for example, in tables 23-22 to 23-24, 10 of the above-mentioned "Perry's Chemical Engineering Handbook", under the item Ammonium Carbamate.

The term "strength welding" and "seal welding", as 15 used in the present description and claims, refer to the following definitions taken from the regulation ASME VIII Div. 1 UW20:

- a strength welding is a welding with such characteristics as to satisfy the project prescriptions, 20 on the basis of the mechanical characteristics and stress deriving from the expansion of the welded parts;
- a seal welding is effected with the purpose of avoiding losses and its dimensions are not determined on the basis of the loads previously ex-

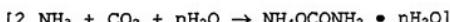
pressed for strength welding.

The pressure equipment according to the present invention can be used for efficiently effecting thermal exchange operations between two mono or multi-phasic fluids, one of which has characteristics of high corrosiveness towards normal carbon steels, and a moderate corrosiveness, also occasional, towards stainless steels. The latter materials are well known to experts in the field and generally consist of alloys based on 10 iron, chromium and carbon, the latter in smaller quantities with respect to common steels. For special applications, certain stainless steels also contain varying quantities of nickel, molybdenum, manganese. The good resistance to corrosion is due to the property of 15 these alloys of passivating in a sufficiently oxidizing environment, by the formation of a surface film of oxide which is inert and mechanically stable. Several examples of these steels are provided, among the numerous publications available, in the above-mentioned "Perry's 20 Chemical Engineering Handbook", from pages 23-39 to pages 23-41 and especially tables 23-10 to 23-15.

The process fluids having a high aggressiveness referred to in the present invention can be monophasic, i.e. usually consisting of one liquid, or multiphasic, 25 normally biphasic, consisting of a liquid phase and a

vapour phase in equilibrium. Typical fluids of this kind are those present in chemical processes such as the production of nitric acid, the production of melamine and particularly those circulating in the high or 5 medium pressure section of a synthesis plant of urea, such as aqueous or aqueous/ammonium carbamate or urea and carbamate solutions present in the carbamate decomposer or stripper, downstream of the reactor, or in the carbamate condenser.

10       The latter equipment normally operates at pressures ranging from 10 to 40 MPa and temperatures from 70 to 300°C, in the presence of mixtures containing water, ammonia, carbon dioxide and ammonium carbamate which is the condensation product of said compounds ac-  
15       cording to the reaction:



The operating conditions are preferably a pressure of 12-25 MPa and a temperature of 120 and 240°C.

20       In the usual industrial plants for the production of urea, to which the present invention particularly refers, the above equipment included in the high or me-  
dium pressure section normally contains volumes ranging from 2000 to 100000 litres.

25       The pressure equipment according to the present invention can have various forms and geometries, both

internally and externally, depending on the function for which it is used. It is appropriately constructed in accordance with the typical criteria of high pressure tube bundle thermal exchangers. It is therefore 5 normally cylindrically shaped with two hemispherical caps at the ends of the cylinder, for a better distribution of the pressure load. Openings are conveniently situated in the hemispherical caps and along the cylindrical body for the entrance and exit of the fluids, 10 the introduction of possible sensors and an opening for inspections (man hole). Depending on the use, it can also be positioned horizontally, as for example in the case of a condenser for carbamate, or vertically, as in the case of a stripper.

15       The external wall of the apparatus, which resists almost all of the pressure load, consists of a thick carbon steel casing, also called pressure-resistant body, having a thickness calculated in relation to the pressure to be resisted and usually varying from 20 to 20 350 mm. In high pressure exchangers, the external wall can conveniently have different thicknesses in relation to the pressure which must be effectively resisted. The central cylindrical zone, in contact with the steam at pressures ranging from 0.2 to 5 MPa, preferably has 25 thicknesses varying from 20 to 100 mm, whereas the wall

of the caps and cylinder close to these, subjected to the usually higher pressure of the process fluids, has proportionally greater thicknesses, preferably from 100 to 300 mm. The outer wall can consist of a single layer 5 or several layers of carbon steel, assembled according to the known art.

Inside the apparatus, there are at least three distinct cavities (or chambers) which are separated from each other by two septa or plates suitably arranged transversally to the main axis of the apparatus, and also comprising a flat carbon steel element, normally having a thickness of 40 to 400 mm, suitable for tolerating the pressure difference usually existing between the cavities defined thereby. In the most common 10 case, the two plates are each situated close to one of the two caps and create a central volume having an essentially cylindrical geometry. Each plate is sealed onto the circular wall by welding, so that there can be no exchanges of material between adjacent cavities. Alternatively, said plates form two cavities situated on the same side of the apparatus, separated from each other by a further septum or plate, as for example in the typical construction technique of the Kettle-type carbamate condenser, in which the two plates are joined 15 in a single transversal plate having one side divided 20 25

in half by a septum welded transversally.

In the tube bundle apparatus object of the present invention, a series of tubes is fixed between the two plates, which are consequently appropriately perforated 5 and commonly called tube sheet plates, so that a fluid can pass between the two cavities situated at the end. A second fluid, preferably a steam/water mixture, is circulated in the intermediate cavity to effect thermal exchange through the wall of the tubes.

10       The number of tubes varies according to the project specifications, but normally varies from a minimum of 2 up to about 10000 for larger equipment. There are preferably from 100 to 5000 tubes, and their diameter ranges from 10 to 100 mm. The length of the tubes usually coincides with the length of the central body of 15 the apparatus and preferably ranges from 1 to 10 m, their shape is generally linear, but tubes comprising curved or toroidal parts are not excluded, and their thickness ranges normally from 2 to 25 mm, according to the load and the tube diameter. Intermediate septa 20 (also called baffles) can be situated in the intermediate cavities to support the tubes. These are generally made of carbon steel and have thicknesses of a few millimetres, as they do not have to resist any pressure 25 load."

According to the present invention, the inner wall of each tube consists of a material highly resistant to corrosion, selected from titanium, zirconium or an alloy of one of them possibly comprising other metals. In 5 a first embodiment, each tube consists entirely of one of said materials, preferably zirconium, and has a thickness ranging from 2 to 15 mm, preferably from 3 to 10 mm.

According to a second embodiment, at least two metallic layers, an external layer, preferably having a greater thickness, consisting of a material relatively resistant to corrosion in the presence of fluids containing passivating agents, such as a stainless steel, which is also suitable for tolerating the difference in 15 pressure between the inside and outside of the tube, and an internal lining layer, preferably thinner, made of said material selected from titanium, zirconium or one of their alloys, which is in direct contact with the corrosive fluid. In this case, the ratio between 20 the thickness of the stainless steel layer and the thickness of the lining layer preferably ranges from 1 to 20, more preferably from 2 to 8. The thicknesses are commonly 1-20 mm, preferably 2-15 mm, for the external layer and 0.5-3 mm for the lining layer.

25 Said bimetallic tubes can be obtained using the

normal metallurgical techniques for the production of metallic linings made of special metals such as zirconium or titanium. A preferred technique is described in the above-mentioned patent U.S. 4,899,813, whose contents are incorporated herein as reference. The lining of said tubes more preferably consists of zirconium with a purity higher than 97%.

The process fluid having a high corrosiveness is situated inside the caps at the end of the apparatus and flows inside said tubes, forming the fluid with a greater pressure. Saturated steam is usually fed into the intermediate cavity at pressures varying from 0.2 to 5 MPa, which, on condensing, releases the necessary quantity of heat, for example, for decomposing the carbamate.

At least one of the cavities in which the inside of the apparatus according to the present invention is subdivided, is put in contact with a fluid which is highly corrosive, under the usual process conditions, not only towards normal carbon steel but also towards stainless steels normally used in the art, even though in this case the corrosion effects can become manifest after cycles of a certain duration. The Applicant has found that it is possible to guarantee the safety and reliability with time of the equipment subjected to

such heavy conditions of use, by either totally or partly effecting the construction of said cavities exposed to corrosion by means of the above structure comprising at least three layers of a different material.

5 According to a preferred aspect for greater economic advantages, it is possible, in fact, to use the three-layered structure only in the areas exposed to major risk of corrosion, still obtaining however an apparatus with the excellent characteristics indicated above.

10 In accordance with the present invention, the layer (A) essentially consists of carbon steel and can at least partly coincide with the external casing of the head. The thickness of this layer depends on the maximum operating pressure of the apparatus and preferably varies from 20 to 500 mm. It can also have different thicknesses in correspondence with different points of the same cavity, such as for example, the thickness of the layers forming the perforated plate with respect to the thickness of the head. In particular, the thickness of the layer A of the perforated plate preferably ranges from 40 to 500 mm, whereas that of the external wall is usually less and preferably ranges from 40 to 350 mm.

15

20

The carbon steels which form the layer A are typically selected from those normally used in the metal-

lurgical field as construction material with high mechanical properties such as elasticity, ductility and hardness (see for example the above-mentioned publication "Perry's Chemical Engineering Handbook", pages 23-5 15).

A second laminar layer B consisting of stainless steel is arranged on at least a part of the surface of the layer A of said cavity. The thickness of the layer B preferably ranges from 1 to 40 mm, more preferably 10 from 3 to 25 mm. Stainless steels suitable for the production of the layer B are generally those with a high resistance to corrosion, typically those mentioned above. Stainless steels suitable for the purpose are, for example, AISI 316L steel, INOX steels, especially 15 25/22/2 Cr/Ni/Mo, special austenitic-ferritic steels, and others usually known to experts in the field. The selection of the most suitable material can be left to experts in the field, on the basis of the performances desired during the operation. Typical examples of said 20 steels are those commercially available under the following trade-names: "2 RE 69" (@, SANDVIK), "724 L" (@, AVESTA), "725 LN" (@, AVESTA), "DP 12" (@, SUMITOMO).

According to the present invention, not all of the 25 internal surface of the cavity in contact with the cor-

rosive process fluid should necessarily consist of said three layers A, B and C but, if necessary, certain areas or parts of the surface can consist of layers A and C alone, closely connected with each other. Experts in 5 the field can determine, during the project, whether said cavity can be entirely or partially bordered by a three-layered wall according to the present invention, on the basis of the data and tests available for the process and equipment in question. On the basis of ob-10 servations made of the most critical areas, at least 25%, preferably at least 40% of the surface of said cavity is usually bordered by a three-layered struc-ture.

According to a simplified embodiment of the pres-15 ent invention, it has been found that it is sufficient for the tube sheet plate alone to consist of said three-layered structure, whereas the remaining surface of the cavity (or head, typically hemispherical) can conveniently consist of layers A and C alone. In this 20 way, a simplified and less costly structure is obtained, which in any case allows the desired results to be achieved as it helps to improve the performances in the more critical areas.

According to a preferred aspect of the present in-25 vention, said cavity in contact with the process fluid

is entirely bordered by said three-layered wall A-B-C, suitably shaped, which has the further advantage of guaranteeing the structural continuity of the whole apparatus.

5        When the exchanger comprises bimetallic tubes, for example of the type mentioned hereinabove, the B layer is strength welded to the stainless steel layer of each of them near the outlet on the surface of the tube sheet plate, in such a way as to secure the seal with respect to the underlying carbon steel and resist the axial stress of the tube. In accordance with the present invention, it is not necessary for the layer B and steel of the bimetallic tube to be made of the same material, but they should be appropriately compatible to allow them to be welded together. The carbon steel and various stainless steels can generally be strength welded to each other with satisfactory results in terms of seal and load tolerance. On the other hand, when at least some tubes of the tube bundle are entirely made 10 of a material selected from titanium, zirconium or an alloy thereof, said B layer on the tube sheet plate acts essentially as a protective intermediate layer, whereas the tubes are preferably strength welded to a suitably shaped C layer.

15        According to the present invention, said third

layer C is arranged on said layer B, in close contact therewith. It consists of a metallic material selected from titanium, zirconium or one or their alloys, preferably zirconium or one of its alloys containing at least 90% by weight of zirconium, more preferably pure zirconium. Said layer C forms a cover or internal lining of the wall of the cavity in direct contact with the process fluid. It has a thickness which is suitable for tolerating mechanical and thermal stress for long periods during use; it preferably has a thickness ranging from 0.2 to 10 mm, more preferably from 0.5 to 5 mm. Possibly, the thickness of the layer C, as well as that of the layers A and B, can also be different in different areas of the apparatus or even of the same cavity, depending on the different geometry, different load or characteristics of the fluid in contact therewith. In particular, on the tube sheet plate the thickness of the C layer is advantageously close to that one of the corresponding layer of titanium, zirconium or an alloy thereof in the tube bundle. Therefore, it ranges preferably from 0.2 to 4 mm, more preferably from 0.5 to 3 mm, in the presence of bimetallic tubes, wherein the C layer is seal welded to the inner layer thereof. When said tubes entirely consist of one of the said non-ferrous metals or alloys, the C layer is pref-

erably strength and seal welded to the tubes and its thickness ranges from 2 to 10 mm, preferably from 3 to 5 mm, Titanium, zirconium and their alloys with certain other metals are known to be among the most corrosion-resistant metallic materials. In addition to pure metals, Ti-Zr alloys and anticorrosive alloys of titanium or zirconium with other metals can be used in accordance with the present invention. Some of these materials are commercially available in formats suitable for 10 the preparation of linings according to the usual metallurgical techniques. References to titanium, zirconium and their alloys are made, for example, in the above-mentioned "Perry's Chemical Engineering Handbook", pages 23-50, tables 23-19. In general, it is 15 preferable for the layer C to consist of the same metal or alloy which forms the internal lining of the bimetallic tubes of the tube bundle, more preferably it consists of zirconium.

The layer C generally consists of a metallic material which cannot be welded with the materials forming said layers B and A, and it is therefore arranged in contact with, resting on or penetrated with these, but not welded onto their surface. When the layer B is only present in certain areas of the wall of said cavity, as 25 for example in the above-mentioned case of the tube

sheet plate in the high pressure stripper in the synthesis of urea, said layer C, which on the contrary preferably extends on the whole surface exposed to corrosion of the cavity and forms the first protective lining, can form a double layer A-C with the underlying carbon steel in the remaining area. The thickness of the layer C in this latter case is preferably greater than that situated on the three-layered wall.

In the area of the tube sheet plate, the layer C 10 is seal welded with the internal lining of each bimetallic tube, in order to prevent contact between the process fluid and underlying layer B. Suitable techniques for this welding are generally known to experts in the field and are illustrated in more detail 15 below.

The structure of the three-layered wall according to the present invention surprisingly allows a series of drawbacks remaining unsolved by experts in the field, to be overcome. When the tube bundle is made of 20 bimetallic tubes, the strength welding of these latters with the stainless steel layer B on the tube sheet plate ensures the structural consistency of the apparatus, while the arrangement of the subsequent layer C made of a material analogous to that of the internal 25 lining of the tube, ensures a long-lasting seal and

protection from the process fluid. In the absence of the C layer, the particular aggressiveness of the fluids in the area of the tube sheet plate, together with a particularly complex geometry, makes the resistance 5 of stainless steel alone insufficient and results in an unsatisfactory duration with respect to the desired productive cycles. On the other hand, the use of the layer C alone on the layer A, without the layer B, would create considerable difficulties for the strength 10 welding of the bimetallic tube which could not be effected on the metal of layer C, due to its incompatibility with stainless steel. Moreover, when the tubes are entirely made of titanium, zirconium or an alloy thereof, a C layer with a suitable thickness allows an 15 adequate strength welding to be obtained to each tube, while the intermediate layer B provides a satisfactory safety level in case of leaking, particularly along the said weldings.

According to a preferred aspect of the present invention, small-sized holes called weep-holes are produced in certain points of the wall of the pressure-resistant body which borders each cavity in contact with the corrosive fluid, with the purpose of revealing 20 possible losses of the internal lining before the carbon steel of layer A undergoes significant damage due 25

to corrosion. A weep-hole normally consists of a small tube having a diameter of 8-15 mm made of corrosion-resistant material, which is inserted in the pressure-resistant body until it reaches the contact point between the latter and the lining consisting of alloy or corrosion-resistant metal. If there is a loss in the lining, as a result of high pressure, the internal fluid, which is corrosive, immediately spreads to the interstitial area between the lining and the pressure-resistant body and, if not detected, causes rapid corrosion of the carbon steel of which the latter consists. The presence of weep-holes allows these losses to be detected. For this purpose, all the interstitial areas beneath the anti-corrosion lining are usually put in communication with at least one weep-hole. The number of weep-holes usually ranges from 2 to 4 for each ferrule.

Although the use of the weep-hole technique has been known for a long time in the art, the particular three-layered structure of the walls of the present apparatus, or part of these, allows the safety of the whole end-product to be improved by producing weep-holes which cross both layers A and B and by lining them with stainless steel. In this way, a possible loss through the fine layer C, due for example to an unex-

pected mechanical abrasion or structural defects of the lining, would bring the corrosive fluid in contact only with the stainless steel which, however, has a sufficient resistance to corrosion as to enable the loss to be detected without there being any significant damage to the structural elements of the pressure-resistant body.

According to a particular aspect of the present invention, a further layer D, of carbon steel, can be possibly inserted between said B and C layer, especially aimed to constitute a suitable surface for the arrangement of the C layer by the known technique of explosive cladding, whereby an explosive charge is blown up on a metallic plate of the C layer to press it onto the underlying D layer at a such very high pressure as to obtain a substantial adherence of the two layers, although no welding between them. The thickness of said D layer is conveniently selected between 2 and 10 mm.

A particular example of the apparatus according to the present invention, relating to a high pressure stripper of a plant for the production of urea, is illustrated below with reference to the drawings provided in the enclosed figures, without limiting however the overall scope of the invention itself.

Figure 1 schematically represents a perspective view of the longitudinal section of a high pressure stripper used for the decomposition of carbamate in a synthesis plant of urea, according to the present invention.

Figure 2 schematically represents a detail of the above Figure 1, relating to the formation of the junction area between said tube belonging to the tube bundle and the lower supporting plate.

Figure 3 schematically represents an analogous detail of the said Figure 2, but relating to the tube sheet plate of a heat exchanger according to the present invention wherein the entire tube bundle is made of zirconium tubes.

For the sake of greater simplicity and figurative clarity of the details, only one tube of the bundle is illustrated in the figures and the dimensions are not proportional to the real dimensions.

The stripper illustrated in figure 1 is positioned vertically and essentially consists of three hollow sections, the upper chamber 1, having a hemispherical shape, the intermediate chamber 3 having a cylindrical shape, through which the tube bundle passes, and the lower chamber 2 having a hemispherical shape. The diameter of the cylindrical section is about 1.5-2 metres

and the length is about 4-6 metres. At the upper and lower end of the apparatus there are two man-holes 7 and 8 respectively, whereas chambers 1 and 2 are separated from chamber 3 by two tube sheet plates 15 and 16 respectively, each having from 1500 to 4000 holes for the discharge of the tubes. The rest of the wall of the two chambers 1 and 2 is bordered by the pressure-resistant body 14.

The solution coming from the synthesis reactor of 10 urea, having a temperature of about 180-200°C and a pressure of about 14-17 MPa, comprising urea, water, excess ammonia, non-converted carbamate, reaches the upper chamber 1 from line 9, and is distributed by means of the toroid 13. The liquid, indicated by the 15 level 17, collects on the bottom of the chamber, and drips into each tube 4 forming a fine layer, whereas vapours of ammonia and carbon dioxide pass through the central part of the tube in countercurrent and are released in the decomposition and stripping phase. These 20 vapours are subsequently discharged through line 10.

The whole internal surface of chamber 1 is lined with stainless steel, for example 25/22/2 Cr/Ni/Mo (urea grade) having a thickness of about 3-10 mm, preferably 5 mm, which has a satisfactory resistance to the 25 process fluids under the existing conditions.

The central section of the apparatus comprises the cylindrical chamber 3, externally bordered by the wall 20 made of carbon steel, usually having a thickness ranging from 10 to 40 mm, through which the tube bundle 5 passes, into which saturated steam is fed, through the inlet 19, at a pressure of about 2-3 MPa and a temperature ranging from 200 to 240°C, which circulates outside the tubes and condenses on the external wall of these, supplying heat to the aqueous solution of urea 10 and carbamate which flows inside. The condensation liquid of the exhausted steam is then discharged from line 18. In this way, the carbamate is decomposed and the excess ammonia vaporized, which also acts as stripping agent. Each tube 4 of the tube bundle consists of an 15 external stainless steel layer, for example 25/22/2 Cr/Ni/Mo (urea grade), having a thickness of about 2-3 mm, internally lined by a non-welded layer of zirconium having a thickness of about 0.7-0.9 mm, and is produced according to said patent U.S. 4,899,813. The relatively 20 fine thickness of the latter allows problems of distortion which normally occur in elements consisting of two metallic layers having very different thermal expansion coefficients, to be avoided, guaranteeing however the desired protection from corrosion. A distributing ferrule 5 having lengths ranging from 200 to 600 mm is in- 25

serted in the upper part of the bimetallic tube, whose purpose is to determine the level of liquid in chamber 1 and its uniform distribution inside the bimetallic tubes.

5        This end 5 of the tube does not require an internal zirconium lining and is normally made of 25/22/2 Cr/Ni/Mo. The remaining part 6 of each tube, which extends along the chamber 3 until it is fixed onto the lower plate 16, is, on the contrary, bimetallic and 10 each end rests on one of the perforated plates by means of a strength and seal welded structure which is described in detail below with reference to figure 2.

The lower chamber 2 is bordered by a pressure-resistant body 14 analogous to chamber 1, and by a 15 lower tube sheet plate 16. The conditions of major aggressiveness and corrosion to the internal wall occur inside this chamber, and especially in the area of the tube sheet plate, where the aqueous solution of urea, coming from the tube bundle, flows. The solution of 20 urea purified for the most part from the carbamate, is collected on the bottom of chamber 2 and is forced into the siphon 11 from which it then proceeds towards the other purification and drying sections. Additional ammonia, if necessary, or carbon dioxide can be charged 25 through the inlet 12, according to an alternative tech-

nology, to favour the stripping. Passivation air is also introduced through the same inlet, when required.

According to the present invention, the wall of chamber 2 (pressure-resistant body and tube sheet plate) comprises three superimposed metallic layers, consisting respectively of carbon steel, stainless steel and zirconium, as illustrated below in more detail with reference to the scheme represented in Figure 2, relating to the conjunction area of a bimetallic 10 tube with a tube sheet plate.

Figure 2 essentially illustrates the section of the pressure-resistant body 21 which forms layer A made of carbon steel, having a greater thickness, usually 100-400 mm, the stainless steel section 22, which forms 15 layer B, on whose surface the lining 23 consisting of a fine zirconium layer C, rests.

The layer 21 in this case coincides with the body of the tube sheet plate 16 and is dimensioned so as to tolerate the stress due to the pressure difference between the lower chamber 2, for collecting the aqueous solution of urea, and the intermediate cylindrical chamber 3, where the steam is condensed. This pressure, for normal urea production processes, ranges from 14 to 18 MPa, preferably 15-16 MPa. Close to a tube 4 belonging to the tube bundle, the layer 21 is suitably perfor-

rated and possibly welded to the tube itself along the edge of the hole.

On the side facing the cavity 2 of the layer 21, there is a laminar layer 22 made of stainless steel which forms layer B according to the present invention. This preferably has a thickness ranging from 3 to 20 mm and in this particular case is made of a "urea grade" stainless steel. "Urea grade" refers to a commercial type of stainless steel with a particular resistance to corrosion of solutions of ammonium carbamate. Austenitic and "urea grade" INOX are among the preferred steels. The laminar layer 22 can consist of laminar elements having a suitable thickness, welded with each other and the underlying layer 21, or, especially in the case of a tube sheet plate, a welding deposit. Near the cross point and discharge into the cavity 2 of a tube of the tube bundle, the layer 22 is strength welded with the external layer 24 of the tube by means of circular welding 26, so that the two layers form a continuous and sealed structure with respect to the carbon steel of layer 21.

The layer 23 consisting of the anticorrosive lining C of the present invention, rests on the surface of the layer 22 facing the cavity 2. This preferably consists of zirconium with a thickness ranging from 2 to 3

mm. The layer 23 is arranged so as to perfectly adhere to or penetrate the surface of layer 22. This is obtained with various welding methods (not usable in this case) such as, for example, explosive cladding, or 5 thermal spraying.

Close to the discharge of each bimetallic tube 4, said layer 23 is superimposed with respect to the welding 26 of the stainless steel layer B and is directly joined with the internal lining 25 of the tube by means 10 of seal welding 27, arranged around the discharge hole. A part of the lining 25 is preferably extended for a few centimeters beyond the layer 23 to favour the dripping of the liquid.

According to a particular aspect of the present 15 invention, a certain number of weep-holes (schematically indicated with by reference 28 in Figure 2) are produced through layers 21 and 22 (i.e. A and B) of the wall of the cavity 2, both laterally in the tube sheet plate and in the wall of the head, protruding below the 20 layer of lining 23. These weep-holes are produced according to any of the various techniques normally in use and are internally lined with stainless steel or even with the same material as layer 23.

In Figure 3 essentially the same features are 25 shown as illustrated and numbered according to Figure

2, but tube 4 entirely consists in this case of a cylindrical zirconium wall 29, having for example a thickness of 4-5 mm and a diameter (internal) of 20-50 mm, preferably 30-40 mm, capable to resist the pressure  
5 difference of about 15-16 MPa between the inner and outer fluids.

Near and around its outlet in the lower cavity, each tube 4 is strength and seal welded to the layer 23 of the tube sheet plate, which constitutes the inner 10 lining the cavity itself, by mean of the welding 31 arranged all around the outlet hole and all along the tube-plate contact surface. According to a particular embodiment of the present invention, a further carbon steel layer 30 (D layer), having a thickness of from 1 15 to 3 mm, is placed and welded on the surface of said stainless steel layer 22, in order to facilitate, in the construction of the equipment, the step of laying the zirconium lining layer 23 by mean of the known technique of explosive cladding. In this case, the 20 weep-holes made in the area of the plate or the head wall comprising the said four layers, are conveniently extended through the layer 30 to reach the surface underlying the lining layer 23.

A second aspect of the present invention relates  
25 to a method for the production of said tube bundle ap-

paratus with enhanced performances.

In accordance with this, the method for the production of the tube bundle apparatus according to the present invention, especially suitable for effecting 5 thermal exchanges between fluids of which one has a high chemical aggressiveness, comprises the construction of a hollow body with an external casing, or pressure-resistant body, appropriate for tolerating the operating pressures and consisting of a material subject 10 to corrosion by contact with said highly aggressive fluid, and the formation, inside said hollow body of at least two cavities separated from each other by a third seal cavity with respect to these, by the interpositioning of at least two plates, or septa, hinged to the 15 pressure-resistant body, on which, to put said cavities in communication with each other, a series of tubes is inserted, forming a tube bundle, whose internal wall consists of a material selected from titanium, zirconium or an alloy of one of these, highly resistant to 20 corrosion, so that during use, said internal wall of the tubes and the wall of at least one of said two cavities is in contact with said highly aggressive fluid, said method being characterized in that the wall which borders at least one of said cavities is at least 25 partly produced by superimposing the following three

metallic layers in order:

- A) an external layer suitable for tolerating the pressure load, subject to corrosion by contact with said highly aggressive process fluid;
- 5 B) a stainless steel intermediate layer;
- C) an anticorrosive layer constituting a lining situated on the internal surface in contact, during use, with said highly corrosive fluid, consisting of a material selected from titanium, zirconium or
- 10 an alloy of one of these, seal welded with the internal wall of each of said tubes.

The whole wall which borders said cavity in contact with the highly aggressive fluid is preferably made up of the above three-layered structure.

- 15 In the preferred case of the production of a stripper for the urea solution, said cavity in contact with the corrosive fluid is the lower one, whereas the upper cavity, in contact with the solution of urea and carbamate under blander conditions, does not require
- 20 the three-layered structure, but consists of layers A and B only.

In a preferred embodiment of the present invention, said method of production comprises the arrangement of a bundle of bimetallic tubes, as previously described.

The production of the anticorrosive lining which forms layer C according to the present invention, can be effected according to any of the suitable metallurgical techniques known in the art, such as, for example, the positioning, on the surface of the layer B, of laminar elements made of the preselected metal or alloy, suitably cut and shaped to adapt themselves to the form of the surface to be covered. The elements are arranged side-by-side and subsequently seal welded to each other. Grooves, supports, connecting elements and other devices or end-products are situated, especially along the edges to be welded, according to the normal procedure known to experts in the field. Welding methods of metals such as zirconium, titanium and their alloys, although less common than the welding of steels, are known and can be easily applied.

According to an embodiment of said manufacturing method, with respect to the wall of the lower cavity of a high pressure stripper for the decomposition of carbamate and the purification of a solution of urea, a second layer B consisting of stainless steel plates resting on the pressure-resistant body and anchored thereto by means of a welding process, is applied to the pressure-resistant body A essentially consisting of carbon steel plates calendered and welded. The thick-

ness of these plates preferably ranges from 3 to 10 mm, and is more preferably 5 mm. Said plates are cut and welded by the edges, according to the usual manufacturing technique of linings for equipment used in the synthesis of urea, to an underlying stainless steel welding deposit applied to fill a series of grooves having a depth of about 3 mm and a width of about 20 mm, previously produced on the carbon steel surface with a suitable geometry corresponding to the shape of the plates. Below the grooves, at an adequate distance between each other, preferably from 500 to 1500 mm, a certain number of weep-holes are subsequently produced in the pressure-resistant body and through said welding deposit, reaching the surface of the latter, with the purpose of monitoring losses during the running of the apparatus.

In a second preferred manufacturing phase, a small zirconium plate, acting as a support, is positioned on said welding deposit, in the space left free by the stainless steel plates. Additional zirconium plates having a varying thickness as described above, not less however than 3 mm, are subsequently applied and welded to each other and onto the underlying zirconium support until the surface of the lower cavity (or bottom) of the stripper is entirely covered. The welding technol-

ogy of this metal, as also titanium and its alloys, is known, but is generally more complex than that of steel and must be carried out in a stream of inert gas, normally argon. The weep-holes also have the advantageous 5 function in this phase of ensuring the necessary protection of inert gas to the underlying surface of the zirconium plate, by means of insufflation with argon.

The production of the tube sheet plate of said lower cavity with the three-layered structure according 10 to the present invention, is preferably effected with a variation of the method described above, which also forms a part of the present invention. In particular, it comprises the following construction phases in succession.

15 A series of holes having adequate dimensions for receiving the tubes destined for effecting the thermal exchange are produced on the tube sheet plate, whose sizes depend on the project specifications, but usually consisting of a circular septum essentially made of 20 carbon steel (resistant body) having a thickness ranging from 300 to 350 mm. The tube sheet plate is then lined, on the side facing the lower cavity, with a layer B consisting of a welding deposit made of stain- less steel 25/22/2 Cr/Mo/Ni by means of the usual weld- 25 ing processes (for example submerged-arc welding). The

tubes are subsequently inserted into the holes produced above. If the tubes are of the said bimetallic type, made up of an external stainless steel layer and an internal zirconium layer, the external layer of each tube  
5 is then strength welded with the above layer B, followed by a suitable mechanical processing of the surface of the tube sheet plate to allow the positioning of the subsequent zirconium layer or to ensure an effective and long-lasting protection of the corrosion to  
10 the underlying inox steel layer. If the tubes are entirely made of one metal or metallic alloy, said layer B is arranged tightly around each tube, and, if required, can be seal welded to it by the known special methods suitable for this aim.

15 In the subsequent phase, after processing the tube sheet plate, one or more zirconium plates of suitable thickness (free lining), sized and shaped so as not to block the outlets of said tubes, are laid on the surface. These are subsequently connected to each other,  
20 with the protrusion of the internal zirconium layer of the bimetallic tubes by a seal welding which seals the whole surface of the plate exposed to contact with the process fluid. If the tubes are entirely made of one of said highly corrosion resistant metals or metal alloys,  
25 for example of zirconium, the C layer, usually up to 10

mm thick, is strength and seal welded to the whole outlet zone of the tube.

In the welding phase, all the interstitial surfaces are preferably protected by an atmosphere of argon through suitable weep-holes produced in the tube sheet plate with a technique analogous to that described above.

According to a particular embodiment of the method according to the present invention, which has never been applied to this type of tube bundle equipment destined for use in a corrosive environment and in particular strippers adopted in synthesis plants of urea, said zirconium layer C on the surface of the lower cavity and plate of the stripper can also be produced by means of one of the thermal spray techniques known in the art. These techniques allow a continuous and uniform layer of a metal, closely connected with the underlying metal, to be laid, by the high temperature spraying of powders or vapours thereof onto the surfaces to be coated. In this way surface coatings having a complex geometry can be obtained, with uniform metallic layers and with the desired thickness, sometimes also much thinner than those obtained by the deposition of plates as described above, with a consequent significant saving in material. Thermal spray techniques

are described, for example, in the publication "AWS Welding Handbook", volume 4, Seventh edition.

According to a preferred aspect of the present invention, said layer C is obtained by means of the spray arc technique. In all the essential variables relating to processes in use, this is a technique which is well-known for applications of hard or anticorrosive deposit on surfaces made of carbon steel or other materials among which austenitic stainless steels, and is used whenever it is necessary to combine mechanical characteristics of toughness in the core of the product, with high resistance properties to erosion or corrosion on the surface, as it forms a close and firm union between the underlying metallic surface and its lining, even if the metals of the two layers cannot be effectively welded to each other. It has never been applied however to the manufacturing of parts of tube bundle equipment in contact with highly corrosive fluids, and in no case in processes for the synthesis of urea, in particular in environments in the presence of carbamate.

According to this technique, the anticorrosive deposit which forms layer C can be effected by means of molten powders or by the application of metallic wires previously melted and consequently sprayed in atomic form onto a metallic surface. Before application it is

preferable to prepare the basic surface either by blasting or any other equivalent surface cleaning technique.

In the particular case described herein, a zirconium deposit thickness is applied on the stainless steel layer of 25/22/2 CrNiMo, ranging from 0.1-10 mm or even more, preferably from 0.5 to 3 mm, depending on the geometry and function of the different zones of the lower cavity of the stripper and the possible subsequent mechanical processing phase of the part in question.

In some cases, these deposits are integrated in their surface layer by various types of "paints", in order to allow the sealing of the inevitable porosities produced by the sprayed or deposited material. The use of sealing paints depends on the nature and type of application process, according to evaluation parameters known to experts in the field.

A further object of the present invention relates to a method for protecting and restoring the surfaces of the tube bundle apparatus in use, subject to strong corrosive attacks, which is simple, economic and reproducible not only in the workshops but also for equipment operating for ordinary maintenance interventions.

25           The improved anticorrosive lining according to the

present invention is also suitable for effecting the functional restoration of pre-existing apparatuses whose original lining needs to be substituted or repaired due to the presence of significant areas of corrosion which jeopardize its functioning and safety. In particular, it is possible to completely restore the original functioning of the apparatus and guarantee, as a result of the enhanced performance of the new lining, a greater operating duration and safety than those of 10 the original ones.

According to a particular aspect of the present invention, the manufacturing method of the above apparatus can therefore also consist in the modification, repairing or revamping of pre-existing equipment. In 15 this case the areas of a tube bundle pressure apparatus effectively or potentially exposed to corrosion, and optionally the whole cavity or part of the apparatus exposed to the risk of corrosion, is entirely lined with the necessary metallic layers until a three-layered structure as described above, is obtained. As 20 an example, which however is non-limiting, in the case of a stripper for the synthesis of urea with a bimetallic tube bundle and lower and upper chambers bordered by a wall and a plate both consisting of a 25 carbon steel pressure-resistant body and a layer of

"urea grade" stainless steel, the reparation method according to the present invention can simply consist in cleaning the whole surface of the lower cavity (by means of the known blasting, reaming techniques, etc.) 5 and the subsequent affixing on the stainless steel layer, of a zirconium layer having the desired thickness, for example from 0.5 to 3 mm, suitably seal welded with the lining of each bimetallic tube.

Other embodiments of the present invention, different from those specifically described above, are 10 however possible and represent obvious variations which are in any case included in the scope of the following claims.

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CLAIMS

1. A tube bundle apparatus suitable for efficiently effecting the thermal exchange, under high pressure and temperature conditions, between at least  
5 two fluids of which one has highly aggressive characteristics under the process conditions, comprising a hollow body equipped with an external casing, or pressure-resistant body, suitable for tolerating the operating pressures and consisting  
10 of a material subject to corrosion by contact with said highly aggressive fluid, and appropriate openings for the entrance and exit of the fluids, inside which there are at least two cavities separated from each other by a third sealed cavity  
15 with respect to these, situated between two septa or plates hinged onto the pressure-resistant body, said two cavities communicating with each other by means of a series of tubes, whose internal wall is put in contact with said highly aggressive fluid  
20 and consists of a material selected from titanium, zirconium or an alloy of one of these which is highly resistant to corrosion, forming a tube bundle situated between said two septa or plates which passes through said third cavity, characterized in that at least one of said two cavities is  
25

in contact with said highly aggressive fluid and  
is at least partly delimited by a wall comprising  
at least three metallic layers consisting of:

- 5           A) an external layer suitable for tolerating the  
              pressure load, subject to corrosion by contact  
              with said highly aggressive process fluid;
- 10          B) an intermediate layer made of stainless steel;
- C) an anticorrosive lining in contact with said  
              highly corrosive fluid, consisting of a material  
              selected from titanium, zirconium or an alloy of  
              one of these.
2.          The apparatus according to claim 1, wherein said  
              material forming the lining C is selected from ti-  
              tanium and zirconium, preferably zirconium.
- 15         3.          The apparatus according to one of the claims 1 or  
              2, positioned vertically, wherein said cavity bor-  
              dered by three layers forms the lower collection  
              chamber of the highly aggressive fluid.
- 20         4.          The apparatus according to any of the previous  
              claims, wherein said three-layered wall completely  
              borders the cavity in contact with the highly ag-  
              gressive fluid.
5.          The apparatus according to any of the previous  
              claims, wherein said layer B has a thickness rang-  
              ing from 3 to 25 mm and said layer C has a thick-

ness ranging from 0.5 to 10 mm.

6. The apparatus according to any of the previous claims, wherein said layer B consists of a stainless steel selected from AISI 316L steel, INOX steels, special austenitic-ferritic steels.  
5
7. The apparatus according to any of the previous claims, wherein said layer C is at least partially obtained by means of a welding deposit.
8. The apparatus according to any of the previous 10 claims, wherein said layer C is obtained by means of the thermal spray technology.
9. The apparatus according to any of the previous claims, comprising weep-holes situated in the pressure-resistant body.
- 15 10. The apparatus according to any of the previous claims, wherein each tube in said tube bundle is a bimetallic tube comprising a stainless steel outer layer and an internal lining layer, in contact with the corrosive fluid, consisting of a material selected from titanium, zirconium or an alloy of 20 one of them.
11. The apparatus according to the previous claim 10, wherein, in said bimetallic tube, the ratio between the thickness of said stainless steel outer 25 layer and said internal lining layer ranges from 1

to 20.

12. The apparatus according to the previous claim 11, wherein, said outer layer has a thickness of from 2 to 15 mm, and said internal layer has a thickness of from 0,5 to 3 mm.  
5
13. The apparatus according to any of the previous claims from 10 to 12, wherein said layer B consists of the same material as the external layer of said bimetallic tube and said layer C of the same material as the internal lining of said bimetallic tube.  
10
14. The apparatus according to any of the previous claims from 10 to 13, wherein said wall comprising at least three metallic layers constitutes at least the plate delimiting said cavity in contact with the highly aggressive fluid.  
15
15. The apparatus according to the previous claim 14, wherein said B layer is strength and seal welded with the stainless steel layer of said bimetallic tubes, and said C layer is seal welded with the internal layer of said bimetallic tubes.  
20
16. The apparatus according to any of the previous claims from 1 to 9, wherein each tube of said tube bundle entirely consists of a metal selected from titanium, zirconium or an alloy of one of them.  
25

17. The apparatus according to the previous claim 16, wherein the average thickness of said tube ranges from 3 to 5 mm.
18. The apparatus according to any of the previous claims 16 and 17, wherein said wall comprising at least three layers constitute at least the tube sheet plate delimiting said cavity in contact with the highly corrosive fluid.  
5
19. The apparatus according to the previous claim 18, wherein, in said plate, said layer C is strength and seal welded to each of said tubes and has a thickness ranging from 2 to 10 mm.  
10
20. The apparatus according to any of the previous claims from 16 to 19, wherein a further carbon steel layer D is inserted between said layers B and C, said layer having a thickness ranging from 2 to 10 mm.  
15
21. Use of the apparatus according to claims 1 to 20 in a plant for the synthesis of urea.
- 20 22. The use according to the previous claim 21, as stripper in the high pressure synthesis cycle.
23. A method for the manufacturing of a tube bundle apparatus according to any of the claims from 1 to 20, comprising in succession:  
25 - the construction of a hollow body equipped

with an external casing, or pressure-resistant body, appropriate for tolerating the operating pressures and consisting of a material subject to corrosion by contact with  
5 said highly aggressive fluid;

the formation, inside said hollow body of at least two cavities separated from each other by a third sealed cavity with respect to these, by the interpositioning of at least  
10 two plates, or septa, hinged to the pressure-resistant body, on which, to put said cavities in communication with each other, a series of tubes is inserted, forming a tube bundle, whose internal wall consists of a ma-  
15 terial selected from titanium, zirconium or an alloy of one of these, highly resistant to corrosion, so that during use, said internal wall of the tubes and the wall of at least one of said two cavities is in contact with  
20 said highly aggressive fluid;

said method being characterized in that the wall which delimits at least one of said cavities is at least partly produced by superimposing the following three metallic layers in order:

25 A) an external layer suitable for tolerating the

- pressure load, subject to corrosion by contact  
with said highly aggressive process fluid;
- B) a stainless steel intermediate layer;
- C) an anticorrosive lining situated on the internal  
surface in contact, during use, with said highly  
corrosive fluid, consisting of a material se-  
lected from titanium, zirconium or an alloy of  
one of these.
- 5            24. The manufacturing method according to the previous  
claim 23, wherein the wall of said cavity in con-  
tact with the highly aggressive fluid is entirely  
produced by superimposing said metallic layers A,  
B and C.
- 10            25. The manufacturing method according to any of the  
previous claims 23 and 24, wherein said layer C  
consists of zirconium.
- 15            26. The manufacturing method according to any of the  
previous claims from 23 to 25, wherein said cavity  
delimited by a three-layered wall A, B and C forms  
the lower chamber of a stripper.
- 20            27. The manufacturing method according to any of the  
previous claims from 23 to 26, wherein said layer  
C is deposited in close contact with said layer B  
by means of a thermal spray technique.
- 25            28. The manufacturing method according to the previous

- claim 27, wherein said thermal spray technique is used in the area of the tube sheet plate.
29. The manufacturing method according to any of the previous claims 27 or 28, wherein said thermal spray technique is a spray arc technique.
30. The manufacturing method according to any of the previous claims from 27 to 29, wherein before the application of layer C, the surface of layer B is subjected to a cleaning step, preferably by means of blasting.
31. The manufacturing method according to any of the previous claims from 23 to 30, wherein said layer C has a thickness ranging from 0.5 to 10 mm.
32. The manufacturing method according to any of the previous claims from 23 to 31, wherein said wall made by three superimposed layer constitute the plate wherein said tube bundle is inserted.
33. The manufacturing method according to any of the previous claims from 23 to 32, wherein said tube bundle is formed by bimetallic tubes, each comprising a stainless steel outer layer and an internal lining layer, in contact with the corrosive fluid, consisting of a material selected from titanium, zirconium or an alloy of one of them.
- 25 34. The manufacturing method according to any of the

previous claims 32 and 33, wherein said B layer is strength and seal welded with the said stainless steel layer of said bimetallic tube, and said C layer is seal welded with the internal lining  
5 layer of said bimetallic tube.

35. The manufacturing method according to any of the previous claims from 23 to 32, wherein said tube bundle is formed by tubes entirely made of a metal selected from titanium, zirconium and an alloy  
10 thereof.
36. The manufacturing method according to a the previous claim 35, wherein, in said plate, said layer C is strength welded with each tube of said tube bundle.
- 15 37. The manufacturing method according to any of the previous claims 35 and 36, wherein a further carbon steel layer D is placed onto said layer B, and said layer C, having a thickness of from 2 to 10 mm, is explosive cladded onto said layer D.
- 20 38. A modification method of pre-existing equipment in order to obtain an apparatus according to any of the previous claims from 1 to 10, said apparatus being a tube bundle pressure apparatus comprising bimetallic tubes made of stainless steel internally lined with a metal selected from zirconium,

titanium or an alloy of said metals, wherein at least a part of the surface in contact with the process fluid is subject to strong corrosive attacks, comprising the application of an internal 5 lining close to and above the areas effectively or potentially exposed to corrosion and optionally on the whole cavity or part of the apparatus exposed to the risk of corrosion, with the necessary metallic layers obtaining a three-layered structure 10 consisting of:

- A) an external layer suitable for tolerating the pressure load, subject to corrosion by contact with said highly aggressive process fluid;
- B) a stainless steel intermediate layer, strength 15 and seal welded with the stainless steel inlet of each of staid bimetallic tubes forming the tube bundle;
- C) an anticorrosive lining situated on the internal surface in contact, during use, with said highly corrosive fluid, consisting of a material selected from titanium, zirconium or an alloy of 20 one of these, seal welded with the internal lining of each of said bimetallic tubes.

39. The modification method according to claim 22, 25 suitable for the repairing or revamping of said

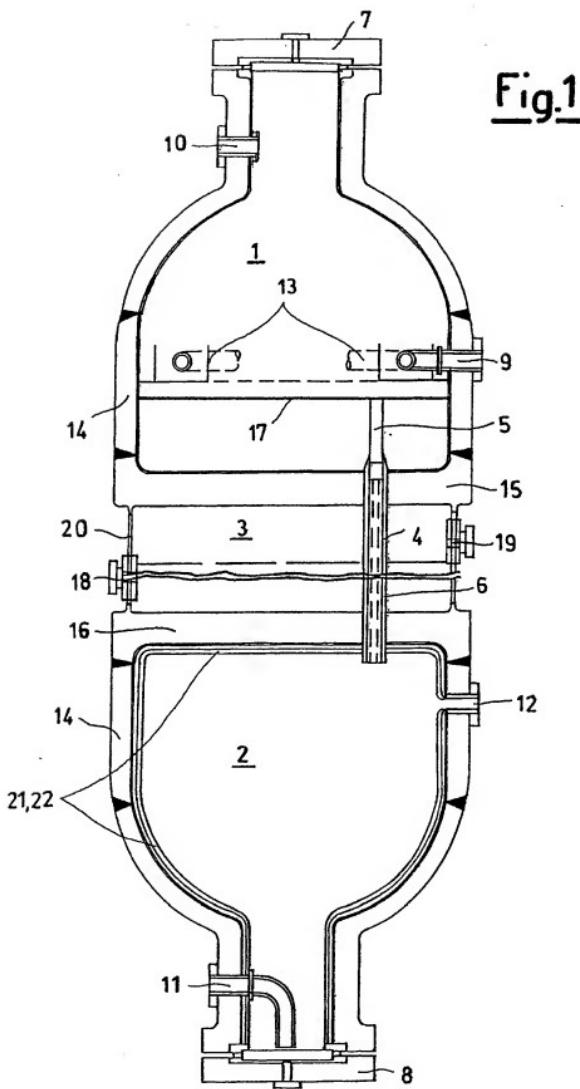
pre-existing equipment.

40. The modification method according to one of the previous claims 22 or 23, effected during an ordinary maintenance intervention.

5 41. The modification method according to any of the previous claims from 22 to 24, comprising the cleaning of the whole surface of the cavity and the subsequent affixing, on the stainless steel layer, of a layer of zirconium having the desired thickness, preferably from 0.5 to 3 mm, suitable seal welded with the lining of each bimetallic tube.

10

1/2



2 / 2

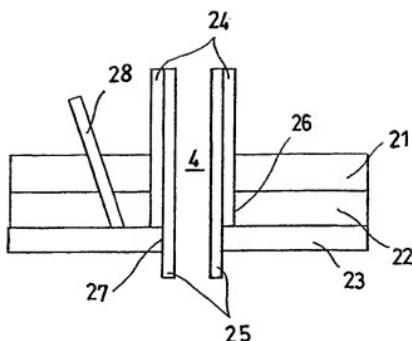


Fig.2

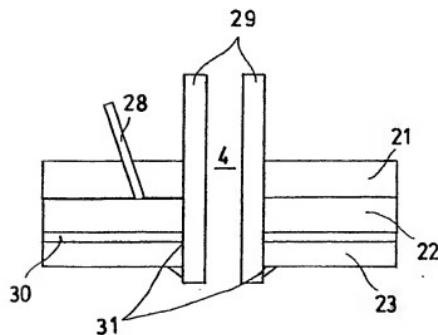


Fig.3

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/04949A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01D19/02 B01J19/24 F28F19/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01D B01J F28F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 899 813 A (GRANELLI FRANCO ET AL) 13 February 1990 (1990-02-13) cited in the application the whole document	1,21-23, 38
A	DE 44 06 852 A (NUOVO PIGNONE SPA) 8 September 1994 (1994-09-08) claims; figures 1,2	1,23
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 148 (M-308), 11 July 1984 (1984-07-11) & JP 59 044593 A (MITSUBISHI ARUMINIUMU KK), 13 March 1984 (1984-03-13) abstract	1

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*'A' document defining the general state of the art which is not considered to be of particular relevance
- \*'B' earlier document but published on or after the international filing date
- \*'L' document which may throw doubts on priority, claim(s) or what is to be taken as the publication date of another document or other special reason (as specified)
- \*'O' document relating to an oral disclosure, use, exhibition or other means
- \*'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'G' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the International search report
20 August 2003	27/08/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Paleislaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax. (+31-70) 340-3016	Authorized officer  Van Belleghem, W

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 03/04949

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 260 (M-720), 21 July 1988 (1988-07-21) & JP 63 041795 A (KOBÉ STEEL LTD), 23 February 1988 (1988-02-23) abstract _____	1

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 03/04949

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 4899813	A	13-02-1990	IT AR AU AU BE CA DE ES FR GB GR IN JP LU MX NL NO PT SE SU ZA	1209532 B 240914 A1 572284 B2 4124185 A 902246 A1 1331993 C 3514250 A1 8603288 A1 2563217 A1 2157687 A ,B 850954 A1 164410 A1 60233047 A 85857 A1 160685 A 8501151 A 851574 A ,B, 80322 A ,B 8501859 A 1731045 A3 8502725 A		30-08-1989 27-03-1991 05-05-1988 24-10-1985 21-10-1985 13-09-1994 07-11-1985 16-04-1986 25-10-1985 30-10-1985 25-11-1985 11-03-1989 19-11-1985 16-12-1985 09-04-1990 18-11-1985 21-10-1985 01-05-1985 21-10-1985 30-04-1992 27-11-1985
DE 4406852	A	08-09-1994	IT AT AT CN DE FR RU	1271958 B 402971 B 40194 A 1096097 A ,B 4406852 A1 2702271 A1 2121123 C1		10-06-1997 27-10-1997 15-02-1997 07-12-1994 08-09-1994 09-09-1994 27-10-1998
JP 59044593	A	13-03-1984	NONE			
JP 63041795	A	23-02-1988	NONE			

# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 60238492  
PUBLICATION DATE : 27-11-85

APPLICATION DATE : 09-05-84  
APPLICATION NUMBER : 59093542

APPLICANT : SUMITOMO METAL IND LTD;

INVENTOR : NAGANO HIROO;

INT.CL. : C23F 13/00

TITLE : METHOD FOR PREVENTING CORROSION OF TITANIUM OR TITANIUM ALLOY

ABSTRACT : PURPOSE: To prevent easily the corrosion of Ti or a Ti alloy exposed to environment contg. nitric acid at a low cost by placing Zr or a Zr alloy in the environment in contact with the Ti or Ti alloy.

CONSTITUTION: Zr or a Zr alloy is placed in environment contg. nitric acid in electrical contact with Ti or a Ti alloy used in the environment. The Zr or Zr alloy having a higher electrode potential than the Ti or Ti alloy is deposited on the surface of the Ti or Ti alloy in the form of a passive film to prevent the corrosion of the Ti or Ti alloy. It is desirable that the surface area of the Zr or Zr alloy is  $\geq$  about 1/50 of the surface area of the Ti or Ti alloy contacting with nitric acid.

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④日本国特許庁 (JP)

⑤特許出願公開

⑥公開特許公報 (A) 昭60-238492

⑦Int.Cl.<sup>4</sup>  
C 23 F 13/00

識別記号 庁内整理番号  
6793-4K

⑧公開 昭和60年(1985)11月27日

審査請求 未請求 発明の数 1 (全3頁)

⑨発明の名称 チタン又はチタン合金の腐食防止方法

⑩特 願 昭59-93542

⑪出 願 昭59(1984)5月9日

⑫発明者 梶村 治彦 尼崎市西長洲本通1丁目3番地 住友金属工業株式会社中央技術研究所内

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⑭出願人 住友金属工業株式会社 大阪市東区北浜5丁目15番地

⑮代理人 弁理士 生形 元重

明細書

1. 発明の名称

チタン又はチタン合金の腐食防止方法

2. 特許請求の範囲

(1) 硝酸環境下で使用するチタン又はチタン合金の腐食防止方法であつて、チタン又はチタン合金に接触する硝酸環境中に、ジルコニウムまたはジルコニウム合金を前記チタン又はチタン合金と接触するように存在させることを特徴とするチタン又はチタン合金の腐食防止方法。

3. 発明の詳細な説明

(1) 産業上の利用分野)

この発明は硝酸環境に晒されるチタン又はチタン合金の腐食を防止する方法に関する。

近時チタン又はチタン合金(以下チタン等と総称する)は、そのすぐれた耐食性の故に、ステンレス鋼にとて代り、例えば硝の酸洗用容器、各種化学工業用機器等の材料として広く使用されるようになつた。チタン等の防食機能は、ステンレス鋼と同様、表面に形成された不動態皮膜による

ものであるが、硝酸溶液中で使用される場合は、使用中にチタン等は、硝酸の強い酸化力によつて酸化を受け、表面に不動態皮膜を形成するから、特別の防食措置をとらないのが通常である。ところが、使用環境が濃硝酸であつても、比較的酸度の薄い方の硝酸、例えば沸騰 8% (41%) HNO<sub>3</sub> のようなものでは、チタン等もかなり全面腐食を受けることが知られている。

(従来技術)

この腐食を防止するため溶液中に酸化剤したとえば O<sup>2+</sup>、CrO<sub>4</sub><sup>2-</sup>、V<sup>4+</sup>などのイオン)を添加する防食法がすでに提案されている(防食技術、Vol. 81, No. 12, P. 769-775 (1982))。従来技術は、硝酸環境下のチタン又はチタン合金の腐食防止に、硝酸溶液に酸化剤を添加して溶液をコントロールしていた。これでは溶液の組成が変化してしまい、硝酸そのものでなくなり、硝酸としての使用ができなくなる。硝酸溶液を後の工程でそのまま使用する場合や、溶液そのものが商品となる場合には、溶液組成が変化してはならないので、溶

液中に酸化剤を入れる方法は利用できない。

(発明の目的)

本発明は、后液側を調整するのではなく、材料側に防食法を適用することによって硝酸中のチタン等のより一層の耐食性の向上を計らうとするものである。

(発明の概要)

本発明者は硝酸濃度においてチタン等より電極電位が貴金属位にあるジルコニウム又はジルコニウム合金をチタン等に電気的に接触させてチタン等の表面に不動態皮膜を形成させることによつて、チタン等の腐蝕環境での耐食性を1段と向上させ得ることを見出した。この場合のジルコニウム、又はジルコニウム合金の層は硝酸浴液に接しているチタン等の表面積の5分の1以上以上の表面積をもつていれば充分であることが判明した。

すなわち本発明は、チタン等に接触する硝酸浴液中に、ジルコニウムまたはジルコニウム合金を前記チタン等と接触するように存在させることを特徴とする。

(実施例と作用)

チタン等の腐食速度に及ぼす硝酸濃度の影響を求めた試験結果を第1図に示す。試験では荷重硝酸中での4.8時間浸漬を2回行つた。第1回に見られる通りチタン等は硝酸濃度が8Nにおいて最も耐食性が劣化することが判明した。

次に8N硝酸環境中のチタン等に純ジルコニア又はジルコニウム合金(ジルカロイ-2)を接触させることによつてチタン等の腐食がどのように阻止されるかを試験した。第1回に使用したチタン、チタン合金、ジルコニウム、ジルコニウム合金の成分を示す。第2図に試験結果を示し、チタン等の腐食速度とそれに接触させたジルコニウムのチタンに対する面積比との影響を示す。第2図よりチタン等の8N硝酸中での防食に必要なジルコニウム又はジルコニウム合金の表面積はチタン等の表面積の5分の1以上あれば防食効果があるりその腐食速度はチタンのみ(ジルコニウムと接触しないとき)腐食速度0.288/m<sup>2</sup>hの8分の1以下に低減することができて装置材料として許容できる値であることが確かめられた。

試験 番号	表面 積 (mm <sup>2</sup> )	H (ppm)	N (ppm)	Zr (wt%)	Al (wt%)	V (wt%)	Ti (wt%)	表面 積 (mm <sup>2</sup> )			
								Br-E <sub>1</sub>	Br-E <sub>2</sub>	Br-E <sub>3</sub>	Br-E <sub>4</sub>
チタン E1	1.6	0.14	5.0	0.19	—	—	—	—	—	—	—
チタン E2	8.0	0.16	6.0	0.17	6.2	4.0	4.0	—	—	—	—

試験 番号	表面 積 (mm <sup>2</sup> )	H (ppm)	N (ppm)	Cr (wt%)	Fe (wt%)	Ni (wt%)	Cr (wt%)	Sn (wt%)	Zr (wt%)	表面 積 (mm <sup>2</sup> )	
										Br-E <sub>1</sub>	Br-E <sub>2</sub>
純ジルコニア E1	6	62.0	2.8	5.0	0.659	0.012	<0.001	—	—	—	—
ジルカロイ-2 E2	6	68.0	8.2	7.9	0.12	0.1	0.06	1.6	2.6	—	—

以上チタンについて防食作用を述べたがチタン合金についても同様の防食効果をあげることができる。

(発明の効果)

本発明の防食方法は、チタン等の硝酸濃度中のチタン等の腐食防止にきわめて有効であり、しかもその実績は容易で低成本であり、したがつて本発明は腐蝕環境下で使用されるチタン等製機器の寿命延長に寄与するところが大きい。

4. 図面の簡単な説明

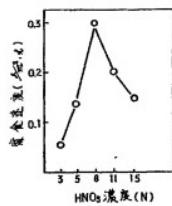
第1図はチタン等の腐食速度に及ぼす硝酸濃度の影響を示す図、第2図はチタン等の腐食速度に及ぼす接触させたジルコニウム又はジルコニウム合金のチタン等に対する面積比の関係を示す図である。

出願人 住友金属工業株式会社

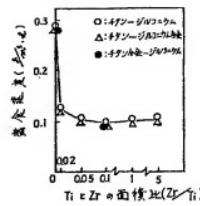
代理人 岩田元重



第 1 図



第 2 図



(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 965 410 A2

(12)

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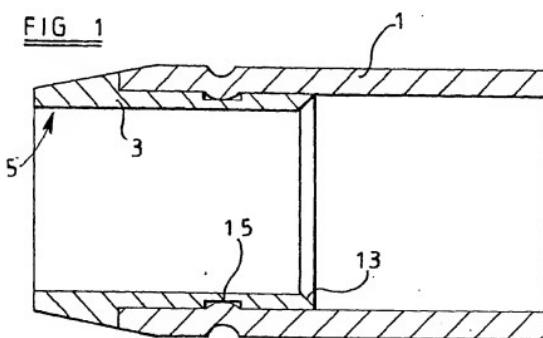
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### (54) Welding shroud and method of manufacture

(57) An electric arc-welding shroud incorporates a high-temperature-resistant metal (3), such as titanium, zirconium or hafnium and alloys thereof, having an oxide coating formed from the metal on at least a part of the

surface thereof. The shroud is made by forming at least part of the shroud of the high-temperature-resistant metal and treating at least the part of the shroud so as to form an oxide coating of the metal on at least a portion thereof.

FIG 1



**Description**

[0001] This invention relates to a welding shroud for electric arc-welding and to a method of manufacturing such a welding shroud.

[0002] Welding shrouds, such as CO<sub>2</sub> welding shrouds, for electric arc-welding are generally made of copper. However, welding shrouds are exposed a harsh environment including high temperatures which give rise to oxidation, mechanical abrasion and spatter from the welding operation which bonds to the copper at the nozzle end of the shroud and can give rise to arcing between the electrode and the end of the shroud.

[0003] A particular problem is the affinity the weld spatter has for copper. The weld spatter builds up at the nozzle end of the shroud and bonds to the copper thus preventing its removal without damaging the shroud.

[0004] The effect of the harsh environment is that known welding shrouds have a short service life and require to be discarded and replaced regularly with attendant high costs.

[0005] It is therefore an object of the present invention to provide a welding shroud for electric arc-welding which minimises the above problems and a method for manufacturing such a welding shroud.

[0006] According to one aspect of the present invention there is provided an electric arc-welding shroud incorporating a high-temperature-resistant metal having an oxide coating formed from the metal on at least a part of the surface thereof.

[0007] According to another aspect of the present invention there is provided a method of manufacturing an electric arc-welding shroud comprising the steps of forming at least part of the shroud of a high-temperature-resistant metal and treating at least the part of the shroud so as to form an oxide coating of the metal on at least a portion thereof.

[0008] The high-temperature-resistant metal may be selected from an element from Group IVA of the Periodic Table and alloys thereof. The high-temperature-resistant metal may comprise titanium, such as ASTM Grade 2 titanium.

[0009] The shroud may incorporate a further metal dissimilar to the high-temperature-resistant metal, such as copper.

[0010] The high-temperature-resistant metal may be in the form of a first tube and the further metal may be in the form of a second tube. The first tube may be secured to the second tube. The first and second tubes may be coaxial, for example with the first tube extending at least partly within the second tube. The first tube may extend axially beyond the second tube in a nozzle region of the shroud. The first tube may extend radially outwardly to cover at least a part of an end face of the second tube where the first tube extends axially beyond the second tube. The outer surface of the first tube may be bevelled in the region where the first tube extends axially beyond the second tube. The first tube may extend with-

in the second tube along part of the length of the second tube. The end of the first tube within the second tube may be internally bevelled.

[0011] The oxide coating may be formed by heat treatment in an oxidising atmosphere. Only the high-temperature-resistant part need be subjected to heat treatment. At least the high-temperature-resistant part of the shroud may be heated to a temperature in the range from 650 to 730 °C, preferably in the range from 680 to 730 °C. At least the high-temperature-resistant part of the shroud may be heated for about 1 to 2 minutes, preferably about 1.5 minutes. At least the high-temperature-resistant part of the shroud may be heated in an oxypropane or oxyacetylene flame or in an oven.

[0012] Alternatively, the oxide coating may be formed chemically, such as by anodisation.

[0013] For a better understanding of the present invention and to show more clearly how it may be carried into effect reference will now be made, by way of example, to the accompanying drawings in which:

Figure 1 is a cross-sectional view through one embodiment of a welding shroud according to the present invention;

25

Figure 2 is a cross-sectional view illustrating one way in which an inner tube of the welding shroud shown in Figure 1 can be made;

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Figure 3 is a partial cross-sectional view of one embodiment of an electric arc-welding torch incorporating the welding shroud of Figure 1;

35

Figure 4 is a partial cross-sectional view of part of another embodiment of an arc-welding torch incorporating the welding shroud of Figure 1;

40

Figure 5 is a partial cross-sectional view of part of a further embodiment of an arc-welding torch incorporating the welding shroud of Figure 1.

[0014] The welding shroud shown in Figure 1 comprises two coaxial tubes in the form of an outer tube 1 and an inner tube 3. The outer tube 1 is made of copper or any other suitable material, although copper is preferred because of its high thermal conductivity which enables the metal to conduct heat rapidly away from the region of the nozzle of the shroud. The inner tube 3 extends from the nozzle end of the shroud and partially along and within the length of the outer tube 1. At the nozzle end of the shroud the inner tube 3 protrudes axially beyond the outer tube 1 and also protrudes radially outwardly to cover the end face of the outer tube 1.

[0015] The inner tube is made of a material different to that of the outer tube and is preferably made of a high-temperature-resistant metal which, when heat-treated, for example in air, forms an oxide layer that has no affinity for the spatter material caused by an electric arc-

welding operation. Suitable metals are those from Group IVA of the Periodic Table, that is, titanium, zirconium and hafnium together with alloys of titanium, zirconium and hafnium.

[0016] Titanium and titanium alloys (especially aluminium, manganese, tin or vanadium) are noted for their ability to form a tenacious oxide coating and can also be anodised to form an oxide layer.

[0017] Zirconium also forms a tenacious oxide scale when heated in air and can be alloyed for example with small amounts of tin, chromium and nickel also copper and magnesium.

[0018] The preferred material for the inner tube 3 is ASTM Grade 2 titanium which has the following composition:

nitrogen up to 0.03 weight percent  
carbon up to 0.10 weight percent  
hydrogen up to 0.015 weight percent  
iron up to 0.30 weight percent  
oxygen up to 0.25 wt percent  
other elements up to 0.30 weight percent (of which each other element is up to 0.05 weight percent)  
balance titanium.

[0019] ASTM Grade 2 titanium provides a cost-effective balance between cost and service life.

[0020] The inner tube 3 is provided with a nozzle portion 5 that is frustoconical in shape. One way in which such a frustoconical shape can be made is illustrated in Figure 2 which shows a tube 7 having a collar 9, of the same material as the tube 7, secured to the tube 7, for example by TIG welding, and a fillet 11 of weld material, again of substantially the same material as the tube 7, fusion welded using a suitable filler wire and a TIG welding process. Indeed, the collar 9 may be secured at the same time the fillet 11 is created. The nozzle portion 5 can then be profiled in a lathe or the like. If desired, a layer of a further high-temperature-resistant metal or other suitable high-temperature-resistant material may be applied to the end of the nozzle portion 5. For example a layer of zirconium may be applied to an inner tube 3 of titanium or titanium alloy, the layer being up to about 2 mm thick and extending along the external frustoconical surface of the nozzle portion for a distance of up to about 4 mm.

[0021] However, it should be noted the inner tube 3 can be made in other ways, including hot working (forging) using well known techniques.

[0022] The other end of the inner tube 3 is formed with an outwardly bevelled portion 13 (that is, the radially outer region of the inner tube is axially longer than the radially inner region thereof) which serves to increase the flow rate of inert gas (such as carbon dioxide) through the shroud to help reduce the temperature.

[0023] The inner tube 3 is provided intermediate the nozzle portion 5 and the bevelled portion 13 with a peripheral recess 15 around the circumference of the outer

surface of the tube, the purpose of which will be explained in more detail hereinafter. If desired, more than one peripheral recess may be provided.

[0024] After the inner tube has been positioned within the outer tube, the inner tube is secured to the outer tube by a rolling operation in which pressure is applied to the outer surface of the outer tube so as to deform material from the inner surface of the outer tube into the recess 15 around the periphery of the inner tube. Deformation of the material of the outer tube into the peripheral recess 15 of the inner tube creates a gas tight joint between the two tubes, while permitting differential expansion. Pressure may be applied, for example, by a rotatable mechanical member or by an hydraulic mechanism. Lateral displacement of the material of the outer tube tends to reduce the overall length of the outer tube and can lead to the end of the outer tube 1 pulling away from the nozzle portion of the inner tube. To counteract this tendency pressure is preferably additionally applied in the region of the junction between the end of the outer tube and the axially adjacent part of the nozzle portion 5 to ensure a close fit between the outer tube and the nozzle portion of the inner tube. For example, for a peripheral recess having an axial dimension of about 3.25 mm and a depth of about 1.25 mm, a rotatable mechanical or hydraulic roller may be used having, for example, a diameter of about 18 mm and an axial dimension of about 2 mm. A second peripheral recess reduces the likelihood of leakage as a result of damage to the seal following contact between the shroud and other components.

[0025] Alternative means (not illustrated) for securing the inner tube to the outer tube may be employed. For example, the outer tube 1 may be provided with an internal thread and the inner tube 3 may be provided with an external thread and the two tubes may be secured together simply by threading the inner tube into the outer tube. As a further alternative, the outer and inner tubes may be made as a single component made of a suitable high-temperature-resistant metal such as titanium, zirconium or hafnium or an alloy of titanium, zirconium or hafnium.

[0026] Prior to insertion of the inner tube 3 into the outer tube 1 to form the welding shroud, the inner tube is heated, for example to a bright red heat (that is, to a temperature in the range from 650 to 730 °C, preferably from 680 to 730 °C) for a time of about 1 to 2 minutes, preferably about 1.5 minutes, with either an oxypropane or an oxyacetylene torch having an oxidising flame to allow the exposed surfaces of the inner tube 3 to absorb carbonaceous gases and oxygen and to form an oxide layer on the exposed surface of the inner tube. The effect of the heat treatment additionally results in surface hardening of the inner tube, reduced ductility and increased strength. Any loose oxide is removed with a wire brush or the like to leave, in the case of titanium, a dull grey oxide surface. As explained above, the oxides of titanium, zirconium and hafnium adhere tenaciously

to the underlying metal and provide a coating to which weld spatter has no affinity. It is therefore relatively easy for an operative to remove weld spatter from the welding shroud from time to time without causing any significant damage to the shroud. Removal of the spatter is effected more easily if the nozzle end and internal surface of the inner tube 3 are relatively smooth in order not to give the spatter an opportunity to key into the inner tube. It is believed that the spatter material, which is generally iron based, assists in maintaining the oxide layer at the nozzle end of the inner tube. Titanium, zirconium and hafnium metals are also non-magnetic which helps to minimise arc wander and plasma deflection. Alternatively, in suitable circumstances the welding shroud as a whole can be heat treated.

[0027] As an alternative to flame oxidation, the inner tube or the entire welding shroud may be heat treated in air or an oxidising atmosphere in a gas or electric oven or by induction heating at a temperature in the range from 650 to 730 °C, preferably from 680 to 730 °C, and for a time of about 1 to 2 minutes, preferably about 1.5 minutes.

[0028] The material of the inner tube continues to oxidise slowly during use so as to maintain a continuous oxide layer thus providing a long service life for the shroud.

[0029] The oxide layer on the inner surface of the inner tube tends to reflect incident radiation, thereby reducing undesired heating of the shroud. Additionally, the copper outer tube demonstrates high thermal conductivity serves to conduct heat efficiently away from the region of the nozzle.

[0030] It should be noted the heat treatment described above is contrary to accepted practice when fabricating reactive metals such as titanium, zirconium and hafnium and their alloys. Previously, it has generally been believed to be essential to exclude oxygen and iron when fabricating such materials.

[0031] Figure 3 illustrates one means by which the welding shroud can be attached to an arc-welding torch 17. In the illustrated embodiment, the internal surface of the outer tube 1 is provided with two axially spaced recesses 19 extending around the internal circumference of the tube. A circlip 21, for example of spring steel, having a substantially circular cross-section, is located in each of the recesses and serves to secure the shroud to the remainder of the welding torch by means of friction.

[0032] The partial cross-sectional view shown in Figure 4 corresponds to part of the view shown in Figure 3. However, in Figure 4 the two axially spaced recesses are replaced by a single recess 23 of greater axial extent and the two circlips are replaced by a single circlip 25 of substantially rectangular cross-section, the greater dimension of the rectangle extending in the axial direction of the outer tube.

[0033] The partial cross-sectional view shown in Figure 5 corresponds to part of the view shown in Figure 3.

However, in Figure 5 the two axially spaced recesses and circlips are replaced by a relatively coarse thread 27 formed on each of the shroud and the remainder of the torch.

- 5 [0034] In one specific embodiment of the invention the outer tube 1 has an axial length of 59 mm, an external diameter of 25.5 mm and an internal diameter of 21 mm. The inner tube 3 has an axial length of 25 mm, an external diameter of 21 mm and an internal diameter of 16 mm which allows sufficient wall thickness to allow for wear as a result of the slow oxidation and for metal depletion resulting from spatter. The nozzle portion extends 7 mm beyond the end of the outer tube giving an overall length of 66 mm and the external frustoconical surface extends at an angle of substantially 20 degrees to the axis of the tube to allow for welding access and to facilitate machining of the nozzle portion. The angle of the frustoconical surface also creates an annular land area on the end of the nozzle portion have a radial dimension of 1 mm. The maximum external diameter of the nozzle portion is about 25 mm. The frustoconical surface additionally extends over part of the outer tube 1, the entire axial length of the frustoconical surface being about 7 mm. That end of the inner tube 3 remote from the nozzle portion may be angled at about 45 degrees to the axis. The peripheral recess 15 has an axial dimension of about 3.25 mm and a depth of about 1.25 mm. Where one peripheral recess is provided the mid-point of this may be about 18 mm from the nozzle end of the inner tube 3. Where a second peripheral recess is provided the mid-point of this may be about 12 mm from the nozzle end of the inner tube.

- 20 [0035] With such a welding shroud the end of the welding tip is advantageously positioned about 4 mm within the nozzle end of the shroud with the result that the nozzle end of the shroud surrounds or covers the area of the weld being formed. The inner tube has the effect of reflecting radiant heat and deflecting spatter and, due to the high-temperature-resistant nature of the material of the inner tube, is able to operate at the high temperatures encountered in welding environments with relatively little risk of damage.

#### 45 Claims

1. An electric arc-welding shroud incorporating a high-temperature-resistant metal (3) having an oxide coating formed from the metal on at least a part of the surface thereof.
2. An electric arc-welding shroud as claimed in claim 1, characterised in that the high-temperature-resistant metal (3) is selected from an element from Group IVA of the Periodic Table and alloys thereof.
3. An electric arc-welding shroud as claimed in claim 2, characterised in that the high-temperature-resist-

- ant metal (3) comprises titanium, such as ASTM Grade 2 titanium.
4. An electric arc-welding shroud as claimed in any preceding claim, characterised in that the shroud incorporates a further metal (1) dissimilar to the high-temperature-resistant metal, such as copper.
5. An electric arc-welding shroud as claimed in claim 4, characterised in that the high-temperature-resistant metal is in the form of a first tube (3) and the further metal is in the form of a second tube (1), the first tube optionally being secured to the second tube.
- 10 6. An electric arc-welding shroud as claimed in claim 5, characterised in that the first tube (3) and the second tube (1) are coaxial.
7. An electric arc-welding shroud as claimed in claim 6, characterised in that the first tube (3) extends at least partly within the second tube (1), in particular the first tube extending axially beyond the second tube in a nozzle region (5) of the shroud.
- 15 8. An electric arc-welding shroud as claimed in claim 7, characterised in that the first tube (3) extends radially outwardly to cover at least part of an end face of the second tube (1) where the first tube extends axially beyond the second tube, the outer surface of the first tube optionally being bevelled in the region where the first tube extends axially beyond the second tube.
- 20 9. An electric arc-welding shroud as claimed in any one of claims 6 to 8, characterised in that the first tube (3) extends within the second tube (1) along part of the length of the second tube, the end of the first tube within the second tube optionally being internally bevelled.
- 25 10. A method of manufacturing an electric arc-welding shroud comprising the steps of forming at least part of the shroud of a high-temperature-resistant metal (3) and treating at least the part of the shroud so as to form an oxide coating of the metal on at least a portion thereof.
- 30 11. A method according to claim 10, characterised in that the high-temperature-resistant metal (3) is selected from an element from Group IVA of the Periodic Table and alloys thereof.
- 35 12. A method according to claim 11, characterised in that the high-temperature-resistant metal (3) comprises titanium, such as ASTM Grade 2 titanium.
- 40 13. A method as claimed in any one of claims 10 to 12, characterised in that at least a further part of the shroud is made of a dissimilar metal (1), such as copper.
14. A method according to claim 13, characterised in that the heat-resistant metal is in the form of a first tube (3) and the further part is in the form of a second tube (1), the first tube optionally being secured to the second tube.
15. A method according to claim 14, characterised in that the first and second tubes (3, 1) are coaxial.
16. A method according to claim 15, characterised in that the first tube (3) extends at least partly within the second tube (1), in particular the first tube extending axially beyond the second tube in a nozzle region of the shroud.
- 20 17. A method according to claim 16, characterised in that the first tube (3) extends radially outwardly to cover at least a part of an end face of the second tube (1) where the first tube extends axially beyond the second tube, the first tube optionally being bevelled in the region where the first tube extends axially beyond the second tube.
18. A method according to any one of claims 15 to 17, characterised in that the first tube (3) extends within the second tube (1) along part of the length of the second tube, the end of the first tube within the second tube optionally being internally bevelled.
- 30 19. A method according to any one of claims 10 to 18, characterised in that the oxide coating is formed by heat treatment in an oxidising atmosphere, for example only the high-temperature-resistant part of the shroud being heated in the oxidising atmosphere.
- 40 20. A method according to claim 19, characterised in that at least the high-temperature-resistant part of the shroud is heated to a temperature in the range from 650 to 730 °C, preferably in the range from 680 to 730 °C.
- 45 21. A method according to claim 19 or 20, characterised in that at least the high-temperature-resistant part of the shroud is heated for about 1 to 2 minutes, preferably about 1.5 minutes.
22. A method according to any one of claims 19 to 21, characterised in that at least the high-temperature-resistant part (3) of the shroud is heated in an oxy-propane or oxyacetylene flame or in an oven.
- 50 23. A method according to any one of claims 10 to 18, characterised in that the oxide coating is formed

chemically, such as by anodisation.

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FIG 1

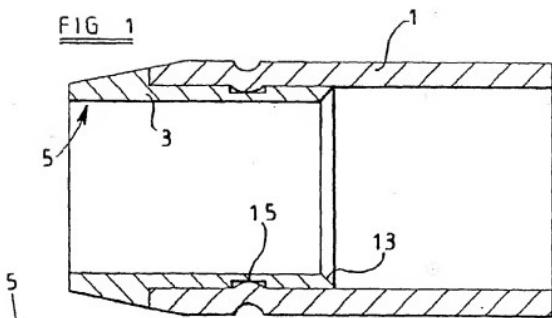


FIG 2

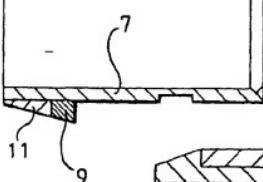


FIG 3

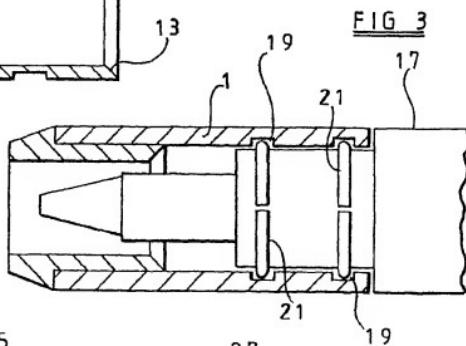


FIG 4

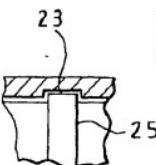
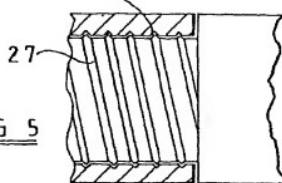


FIG 5



(19)



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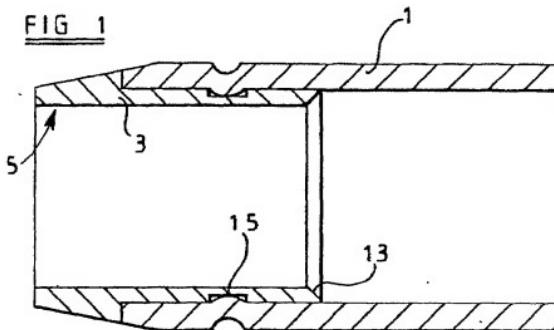
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### (54) Welding shroud and method of manufacture

(57) An electric arc-welding shroud incorporates a high-temperature-resistant metal (3), such as titanium, zirconium or hafnium and alloys thereof, having an oxide coating formed from the metal on at least a part of the

surface thereof. The shroud is made by forming at least part of the shroud of the high-temperature-resistant metal and treating at least the part of the shroud so as to form an oxide coating of the metal on at least a portion thereof.

FIG 1





European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 99 30 3537

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
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	-		TECHNICAL FIELDS SEARCHED (Int.Cl.)
			B23K
<p>The present search report has been drawn up for all claims</p>			
Place of search: <b>THE HAGUE</b>		Date of completion of the search: <b>15 August 2001</b>	Examiner: <b>Herbretreau, D.</b>
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another Document of the same category A : technological background O : non-written disclosure P : intermediate document			
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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15-08-2001

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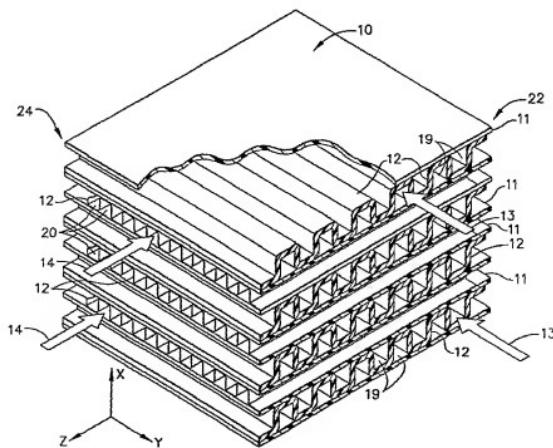
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TITANIUM-BASED HEAT EXCHANGERS AND METHODS OF MANUFACTURE

**WO 02/099352 A1**

(57) Abstract: Oxidation protection of a titanium heat exchanger is provided by a titanium aluminide or solgel coating. The coating protects bare titanium and brazed surfaces of the heat exchanger.

## Titanium-Based Heat Exchangers and Methods of Manufacture

### Reference to Cross-Related Application

[0001] This is a continuation-in-part of U.S. Serial No. 08/865,905, filed on May 30, 1997, now pending.

### Background

[0002] The invention relates to heat exchangers. More specifically, the invention relates to oxidation protection of titanium-based heat exchangers.

[0003] Certain heat exchangers used in aircraft environmental control systems are exposed to temperatures exceeding 400°C. These heat exchangers are typically made of stainless steel, which can withstand the high temperatures.

[0004] It would be desirable to use titanium heat exchangers instead of stainless steel heat exchangers. Titanium and its alloys have a light weight and can provide a weight reduction of up to 40% over comparable stainless steel heat exchangers. The weight reduction results in better fuel efficiency and lower aircraft operating costs.

[0005] However, titanium is not used for high temperature heat exchanger applications because the titanium exhibits a propensity to rapidly oxidize, (over a couple of hours), at the required operating temperatures. Oxidation of titanium results in a reduction in ductility and then strength, and a deterioration in structural integrity. Repeated thermal cycling at temperatures between ambient temperature and around 400°C (and higher) causes the titanium to crack. Cross contamination of fluids can occur and lead to life-threatening conditions.

### Brief Description of the Drawings

- [0006] Figure 1 is an illustration of a core of a titanium heat exchanger.
- [0007] Figure 2a is an illustration of a first method of applying a protective coating to the titanium heat exchanger.
- [0008] Figure 2b is an illustration of a second method of applying a protective coating to the titanium heat exchanger.
- [0009] Figure 3 illustrates a titanium aluminide protective coating.
- [0010] Figure 4 illustrates the importance of the transformation temperature on the oxidation resistance of the coating.

### Detailed Description

[0011] Reference is made to Figure 1. A heat exchanger core 10 includes a plurality of flat parallel plates 11 that are separated by spacers or fins 12. The plates 11 and fins 12 define first and second fluid flow passageways 13 and 14. Dimensions of the passageways 13 and 14 are typically between about 0.5 mm and 2 mm square, and may be about 400 mm long. The passageways 13 and 14 may be designed to promote turbulence in the fluid flow in order to improve heat transfer by the avoidance of boundary layers. Although not shown as such, the passageways 13 and 14 of the heat exchanger core 10 may have wavy shapes or other complex shapes that create turbulence.

[0012] The plates 11 and fins 12 are made of a titanium-based metal. Making the heat exchanger core 10 of titanium offers a 40% weight saving over stainless steel or superalloys that are currently used. Because of its complex geometry the material used to make the heat exchanger must be formable into complex geometries, preferably at room temperature. Titanium, alpha, alpha-plus-beta and beta titanium alloys are preferred.

**[0013]** The fins 12 are bonded to the plates 11 by brazing. During fabrication, the plates 11 and fins 12 and brazing filler metal are stacked to form a stacked assembly. The stacked assembly is then heated to form a brazed and unified core 10. In addition to bonding the plates 11 to the fins 12, the braze maintains integrity of the fluid passageways 13 and 14. Most of the plates 11 and fins 12 are coated with the braze alloy. A large fraction of the surface of the heat exchanger core 10 is braze clad and therefore has a varying chemistry and surface finish.

**[0014]** Typical brazes for titanium and its alloys contain less than 50% titanium, with 20% being usual. Other typical metals in the braze are copper, silver, nickel and zirconium. Some titanium brazes contain no titanium (e.g., a braze including Ag 82% Pd 9% Ga 9%) and many only contain trace amounts of titanium (e.g., a braze including Ag 59% Cu 27.25% In 12.50% Ti 1.25%). Thus a range of alloys are used to braze titanium, and after brazing these alloys will have a composition ranging from that of the braze to that of the titanium alloy.

**[0015]** Manifolds and end plates (not shown) are typically welded to the heat exchanger core 10. The manifolds and end plates are typically not braze coated. Therefore, the manifolds and ends of the fins are usually bare titanium.

**[0016]** The completed heat exchanger has a range of surfaces. Some of these surfaces result from individual manufacturing processes such as casting and rolling. Other surfaces are brazed and welded. Some of these surfaces are inside the heat exchanger and, once formed, cannot be visually inspected or prepared for coating.

**[0017]** A protective coating is applied to exposed surfaces of the heat exchanger core 10, the manifolds and the end plates. The coating may be either a titanium aluminide coating or a solgel coating. The coatings and thermal cycles

are compatible with the titanium alloy and also with the braze alloy. Protection of one, but not the other, would be of no benefit and separate coatings for each are not technically or economically desirable due to the complexity of the heat exchangers shape and the complex transitions from bare to braze clad titanium. Not only do the titanium aluminide and solgel coatings provide oxidation protection, but they are able to withstand the different thermal stresses due to thermal cycling set up by either titanium or braze clad titanium, because of their good bonding to the base titanium and braze, their high strength and because they are thin. The braze and titanium have different coefficients of thermal expansion so locally at the junction between braze clad and titanium the coating may be subject to high strains and stresses.

[0018] Moreover, the coatings maintain adequate strength and ductility in the titanium, which allows the heat exchanger to handle structural forces occurring in high temperature heat transfer applications. In an aircraft, for example, there are high pressures and temperature cycling and vibrations from the surrounding environment (e.g. the aircraft engine on which the heat exchanger is attached). The coatings do not reduce the thermal conductivity of the titanium and, therefore, do not reduce the heat exchanger efficiency.

[0019] Referring to Figure 2a, an exemplary method of creating a titanium aluminide protective coating will now be described. An aluminum conversion coating is applied to the heat exchanger to ensure coverage of all of the exposed surfaces (block 210). The conversion coating may be applied by a mechanical process, such as roll bonding, or by physical vapor deposition (PVD) or low temperature chemical vapor deposition (LTCVD). Preferably the deposited conversion layer has thickness in the range of 0.5-40 microns.

[0020] The preferred technique, however, is applying the aluminum conversion coating as a gaseous phase at a temperature below which aluminum

does not appreciably react with titanium or braze melts (about 500°C). The gaseous deposition may be performed at temperatures below 300°C. An advantage of using gas as a carrier is that the gas flows throughout the heat exchanger at a low pressure and velocity. As a result, heat exchanger surfaces designed to create turbulent gas flow, surfaces at which have stagnant flow areas, and other hard-to-reach surfaces within the heat exchanger are all uniformly coated. Thus the gaseous deposition results in a conversion coating that is applied with a uniform thickness, even if the heat exchanger has a complex geometry.

[0021] The coated assembly is then heat treated (e.g., in a vacuum furnace) to activate the conversion coating and transform the aluminum into titanium aluminide with an alumina surface (block 212). Upon heat treatment, the aluminum oxidizes to form alumina and interacts with the titanium to form the titanium aluminide. The heating and cooling rates are controlled to avoid cracking the titanium aluminide. Cracking of the titanium aluminide coating is a particular concern, as it will result in oxidation of the titanium in the cracked area. As oxygen diffuses quickly in titanium, a single crack can result in the oxidation of a complex heat exchanger part.

[0022] The aluminum conversion layer may be transformed to titanium aluminide by heating at a slow controlled rate above 500°C up to 750°C, followed by a short hold, and cooling at a controlled slow rate down to about 500°C. For example, heating may be at 100°C per hour after 500°C followed by a 30 minutes hold at 750°C and then cooling will also be around 100°C per hour down to 500°C.

[0023] The resulting surface structure of the titanium metal component is illustrated in Fig. 3. The diffusion of aluminum and transformation of titanium

to titanium aluminide preferably occurs at temperatures around 700°C. A conversion layer having thickness in the range of 0.5-40 microns could produce a titanium aluminide coating having a thickness between 1 and 80 microns.

**[0024]** After the low temperature heating, a surface layer of alumina remains on the titanium aluminide. The alumina surface layer also provides oxidation protection. The thickness of the alumina surface layer may be between 0.5 microns and 5 microns.

**[0025]** Correct heat treatment of the protective coating results in an oxidation resistant coating that protects the titanium from oxidation and embrittlement even after exposure for 4,000 hours up to 800°C. This is illustrated in Table 1, which indicates mechanical properties of coated titanium alloy Ti21S, and a simple alloy Ti 3-2.5, which is highly prone to oxidation. Foil of seven mil thick was used. This foil is more prone to oxidation than large heat exchanger sections due to its very high surface area to volume ratio.

Table 1: Mechanical Properties of Ti 21S & Ti 3-2.5 7mil foil after exposure to high temperatures and the associated weight gain due to oxidation

Alloy + Coating	Temp. [°C]	Time [hrs]	YS [ksi]	UTS [ksi]	Elongation [%]	Weight Gain [μg/cm <sup>2</sup> ]
Ti 3-2.5 + Al	700	4,000	41	86	14	-
Ti 3-2.5 + Al	700	4,000	65	83	17	-
Ti21S + Al	700	4,000	115	121	4	-
Ti21S + Al	700	4,000	117	118	5	-
<hr/>						
Ti21S	700	192	70	75	0.5	1160
Ti21S + Al	700	192	117	130	10.7	50
Ti21S	760	192	-	75	~0.0	2600
Ti21S + Al	760	192	109	111	13.6	100

[0026] Table 1 shows the mechanical properties of aluminum-coated Ti21S after exposure to about 700°C and 760°C for 192 hours and 4000 hours.

[0027] Because the preferred gaseous deposition technique is performed at low temperatures, it has several advantages over conventional techniques such as PVD, CVD and in-the-pack and above-the-pack techniques. The conventional techniques involve temperatures (typically about 1,000°C) that would destroy the mechanical properties of the titanium due to grain growth or over-aging, depending on the temperature and alloy. The conventional techniques would also open up the possibility of oxidation of unprotected titanium, even if the process occurs in a vacuum. In addition, conventional techniques involve temperatures above or close to that of the melt temperature of titanium brazes (typically about 900°C). Erosion is a common problem with titanium; it is indicative of too high a braze temperature or too long a time at high temperatures. Even temperatures of about 800°C could lead to a non-optimum

coating and result in erosion and metallurgical problems due to excessive diffusion. In addition, excessive distortion of the complex shape of the heat exchanger would occur, with leaks forming between passages.

**[0028]** Deposition of the aluminum at too high a temperature prevents the formation of the surface alumina layer. Deposition at the elevated temperature results in the diffusion of the aluminum into the titanium during the coating process so afterwards there is no aluminum to oxidize to alumina. Hence, protection would only be provided by titanium aluminide and not by the titanium aluminide and alumina layer. For the braze clad material, dissolution of the aluminum into the braze would be complete and an oxidation protection barrier would not be formed.

**[0029]** The heat treatment temperatures determine the type of titanium aluminides formed and the degree of diffusion of the aluminum into the titanium. The gaseous coating and heat treating steps can be separated to give better control of microstructure and the formation of the alumina layer, unlike conventional processes (in-the-pack and above-the pack processes) that combine the coating and heat treating steps.

**[0030]** Even exposure of aluminum-coated titanium to these high temperatures results in the dissolution of the aluminum plus the formation of undesirable titanium aluminides as Table 2 shows. The titanium alloy Ti21S coated with a thin 10 micron aluminum layer was heat treated over a wide temperature range to illustrate the different aluminides that can be formed. At the higher temperatures, the phases are titanium-rich as the aluminum diffuses into the center of the component. The amount of alumina ( $\text{Al}_2\text{O}_3$ ) decreased by over a factor of five, going from a major constituent to minor as the heat treatment temperature increases. Both of these effects would be expected to reduce oxidation resistance.

[0031] Figure 4 shows that the weight gain after exposure to 600°C for 192 hrs is the same for the material heat treated at 1,000°C as for bare material (see box insert) with no protection. While heat treating at 700°C results in a low weight gain.

Table 2: Comparison of Titanium Aluminide Phases formed and Wt.% of  $\text{Al}_2\text{O}_3$  Vs. Heat Treating Temperature

Temperature [°C]	Titanium aluminide phases	Approx. wt% of $\text{Al}_2\text{O}_3$
700	$\text{Al}_5\text{Ti}$ trace Ti	1
850	$\text{Al}_5\text{Ti}$ , $\text{Al}_2\text{Ti}$ , $\text{AlTi}$ & $\text{AlTi}_2$	0.5
1,000	$\text{AlTi}_3$ , trace $\text{Al}_2\text{Ti}4\text{C}_2$ , & $\text{Al}_5\text{Ti}_2$	0.2

[0032] Referring to Figure 2b, an exemplary method of creating a solgel dip coating will now be described. The solgel dip coating can be applied directly to the titanium or titanium aluminide surface of the heat exchanger by a paintbrush, by spraying or by dip depositing (310). Preferably, the heat exchanger is dipped in a solgel solution for a time period just sufficient to ensure wetting of all the surfaces and removal of any entrapped air. Viscosity of the solgel solution is less than 1 centipoise; otherwise the solution may not enter all the passages of the heat exchanger and will block the passages that it does enter. The low viscosity of less than 1 centipoise also allows for a uniform coating thickness, which reduces cracking of the coating. Withdrawing the heat exchanger at a controlled, predetermined rate also allows for a uniform coating thickness. Increasing the rate will increase the coating thickness. A rate of around 150 mm per min has been found to be satisfactory.

**[0033]** The solgel coating is formed by a reaction of the solgel solution with water usually in the form of moisture in the atmosphere. These reactions occur at room temperature. The coating on the heat exchanger is hydrolyzed and subsequently polymerized in a controlled humidity environment (312).

**[0034]** The coating may be rapidly heated and cooled in an air furnace during application (314). The heating and cooling allow the solgel to be formed in less than an hour (as opposed to one day, which is typical). For example, the solgel coating may be fired by placing it directly in a pre-heated furnace and removed after a roughly 30 min hold. The low temperatures avoid the use of a vacuum furnace for each "drying" step and thereby significantly reduce the cost of applying the solgel protective coating.

**[0035]** The solgel coating is heat treated at low temperatures (316). The heat treatment densifies the coating so that it provides a barrier to oxidation. Low temperatures of about 300°C to 500°C avoid oxidation of the uncoated titanium. Temperatures over 700°C, in contrast, would oxidize the titanium, rendering the heat exchanger brittle and unusable. These high temperatures will result in grain growth and will also overage titanium alloys. They will also result in distortion of the complex shape of the heat exchanger and leakage between passageways 13 and 14.

**[0036]** The solgel coating is preferably applied through multiple dips. For example, the solgel coating may be applied in three dips wherein the coatings of the first and second dips are fired (that is, dried) at a low temperature of 300°C to 500°C (a temperature at which the titanium has minimum or no oxidization) for a 30 minute time period; and the third dip is fired in air or a protective atmosphere at 350°C to 600°C for a 30 minute time period with no oxidation of the titanium. This rapid firing in air is a marked advantage over the typical 700°C to 800°C firing. It makes the process less expensive and more

viable because it avoids the use of a vacuum furnace that would be required for the conventional process and reduces time compared to the conventional process.

**[0037]** Solgel coatings include alumina, zirconia, titanium oxide and silica. These solgel coatings can be readily applied directly to the titanium alloy, the braze or to the titanium aluminide coating to provide oxidation protection. The zirconia and alumina coatings have the advantage of the rapid firing cycle at a low temperature of 350°C to 600°C. Alumina has the advantage of a higher thermal conductivity than zirconia.

**[0038]** These solgel coatings also provide oxidation protection and allow high strength and ductility to be retained in the titanium. This is true even for a 4 mil thick foil of Ti 3-2.5, an alloy very prone to oxidation, after exposure to 600°C for 192 hrs. See Table 3.

Table 3: Mechanical Properties of Zirconia Solgel Coated Ti 3-2.5 After Exposure to 600°C for 192 Hours

Zirconia solgel	YS [ksi]	UTS [ksi]	EI [%]
Ti 3-2.5	80	103	8

**[0039]** The titanium aluminide and solgel coatings may be applied to structures other than heat exchangers. For instance, the coatings may be applied to exhaust manifolds on internal combustion engines and gas turbine engines, titanium impellers, etc.

**[0040]** Although the present invention has been described above with reference to specific embodiments, it is not so limited. Instead, the present

invention is construed according to the claims that follow.

The claims

1. A method of fabricating a heat exchanger (10), the method comprising:  
forming a titanium heat exchanger core; and  
applying a protective coating to bare titanium and braze surfaces of the core (210), the coating being applied by applying an aluminum conversion layer to the core at a temperature below which aluminum does not appreciably react with titanium, and then heat treating the conversion layer so the aluminum oxidizes and interacts with the titanium to form titanium aluminide (212).
2. The method of claim 1, wherein the aluminum conversion layer is transformed to titanium aluminide by heating at a slow controlled rate above about 500°C followed by a short hold at a temperature no more than 750°C, and cooling at a controlled slow rate back down to about 500°C.
3. The method of claim 1, wherein the conversion layer is applied at temperatures below 300°C
4. The method of claim 1, wherein the titanium aluminide coating has thickness in the range of at least 0.5 microns.
5. The method of claim 1, wherein the conversion layer is oxidized to form an alumina surface layer.
6. The method of claim 1, wherein the conversion layer is applied by gaseous deposition.

7. The method of claim 6, wherein the gaseous deposition and heat treating are performed separately.
  
8. A method of fabricating a heat exchanger, the method comprising:  
forming a heat exchanger core;  
applying a solgel solution to the heat exchanger core, the solution having a viscosity of less than 1 centipoise, whereby a coating results (310); and  
sintering the coating at temperatures between about 300°C to 650°C (314).
  
9. The method of claim 8, further comprising rapidly heating and cooling the coating after it is applied to the heat exchanger core.

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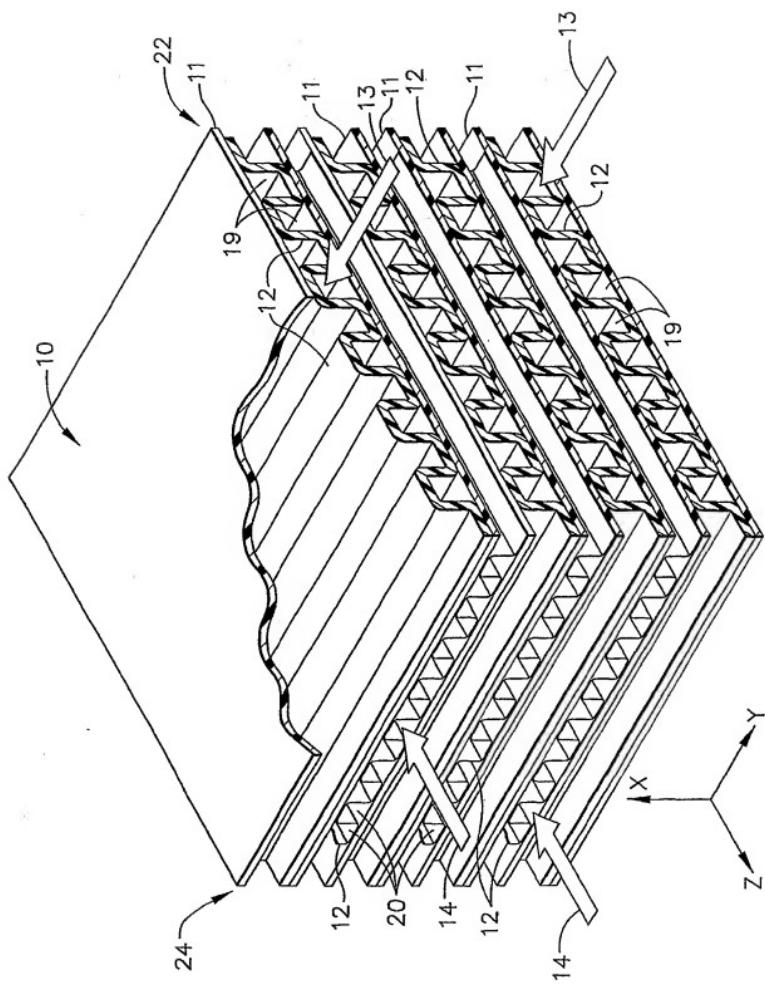


FIG. 1

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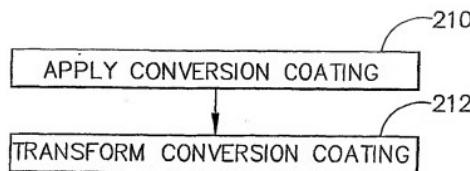


FIG. 2A

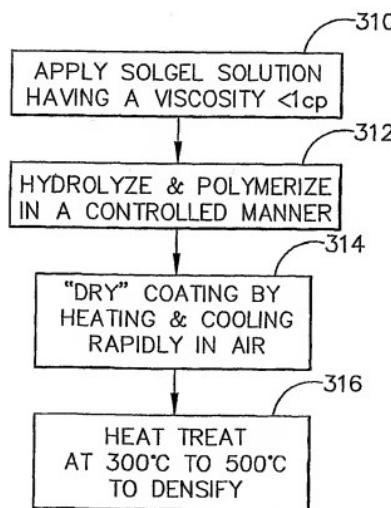


FIG. 2B

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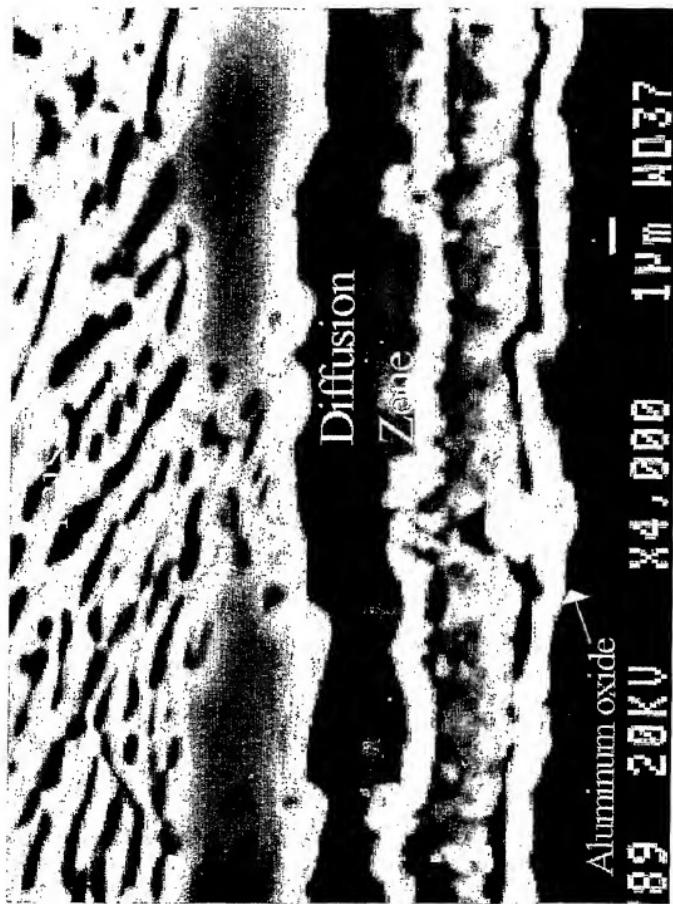


FIG. 3

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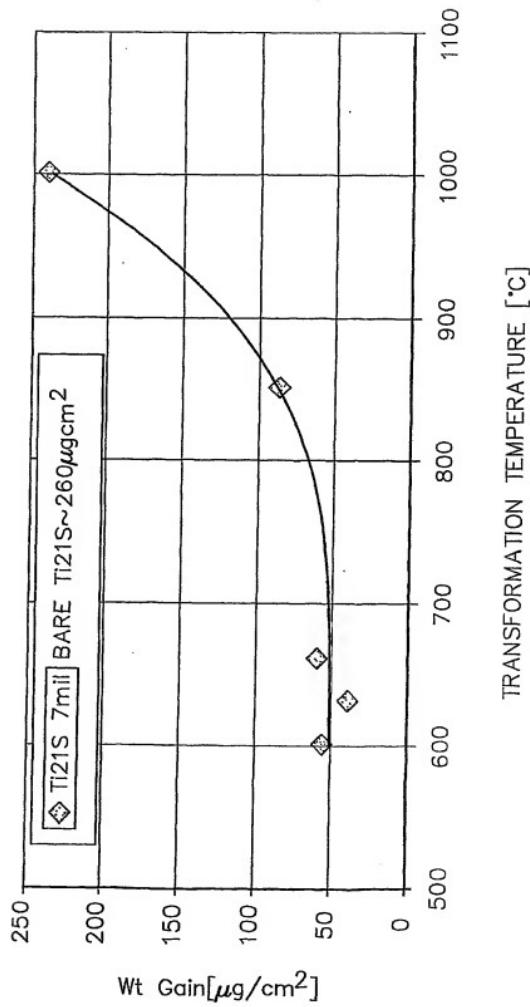


FIG. 4

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/22524

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 F28F19/06 F28F21/08 C23C26/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C23C F28F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 54531 A (ALLIED SIGNAL INC) 3 December 1998 (1998-12-03) page 8, paragraph 2 -page 9, paragraph 2 page 10, line 1 -page 11, line 2; figures	1-9
A	US 4 936 927 A (GRUNKE RICHARD ET AL) 26 June 1990 (1990-06-26) column 3, line 14 -column 4, line 59; figures	1-9
A	EP 0 495 454 A (SUMITOMO LIGHT METAL IND) 22 July 1992 (1992-07-22) page 3, line 7 - line 20	1

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search

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Information on patent family members

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